JOURNAL
OF THE
WASHINGTON ACADEMY OF SCIENCES

VOL. 31 AUGUST 15, 1941 No. 8

PHYSICAL CHEMISTRY.—*Physical reflections in a chemical mirror.*[1] R. E. GIBSON, Geophysical Laboratory, Carnegie Institution of Washington.

Since it is a long-established custom in this Society that the retiring president give an address on some branch of natural philosophy with which he is acquainted at first hand or to which he has actually made contributions, I shall speak tonight about the physical chemistry of solutions. Superficially, a solution is the simplest result we know of the interaction of unlike species of matter and may be defined as follows. When two or more different substances are mixed, we frequently find that a mass is produced that is homogeneous to all macroscopic criteria, whose properties are somewhere intermediate between those of the original components, and from which these components may be recovered by relatively simple operations. Such a mass is called a solution: physically, it acts as a single phase of matter; chemically, its composition is continuously variable within wide limits, a fact that distinguishes it from the orthodox chemical compound.

Although solutions may be solids, liquids, or gases, liquid solutions have claimed most of our attention because of the fact that matter occurs in a relatively dense, readily confinable, but highly mobile form in liquids. Their external mobility, which permits their easy transfer from place to place, and their internal mobility, which makes them highly convenient media for chemical reactions, have given liquids a unique place in the dynamic phases of matter and life.

The main problems connected with a study of solutions seem rather simple and may be stated in the form of the following questions: (1) How can we predict exactly the properties and behavior of a solution from a knowledge of those of its components? (2) What characteristics of a solid and a liquid cause the former to dissolve in the latter? How is solubility influenced by pressure, temperature, and other dis-

[1] Address of the retiring president of the Philosophical Society of Washington delivered at the 1176th meeting of the Society, January 18, 1941. Received July 5, 1941.

solved substances? (3) What types of interaction take place among the molecules of different species intimately mixed in a solution; what deductions about these interactions can we make from observations on solutions and conversely; how do these interactions foreshadow profounder changes that may occur subsequently in the solutions?

Answers to these questions, which really represent particular phases of the general problem of molecular interaction, might enable us to understand the processes going on in the vast solutions that lie *around* us in the oceans, *below* us, transporting materials within the earth, and *within* us, giving us nourishment and forming an essential link in that complex chain of processes we call life. Through the medium of solutions in water, the soul of man finds expression in the creation of beauty or the search for truth, and only through the same media can he appreciate these achievements. There is no doubt of our conscious or unconscious familiarity with solutions. From a more objective point you are well acquainted with solution phenomena; you have all seen salt or sugar dissolve in water; some of you may have studied more complex solutions such as those of alcohol, sugar, and water; you may have been struck by the mystery of a rigid, massive solid being reduced to a state of mobility by mere contact with a liquid; you may have wondered what happened to the solid. So have many hundreds of generations of men before you. Each generation has contributed to our knowledge of the phenomena of solutions, has added some new facts, and each generation has tried to explain these facts. Unfortunately, each generation has been better at discovery than at explanation—has raised more problems than it has solved—and each generation has outgrown the simpler explanations it inherited. The study of solutions has now grown to be very complex; an exact description of the large body of facts that has been accumulated about the properties of solutions in terms of a few simple postulates, in short, a theory of solutions, suffers from the same evil that besets all generalizations about phenomena close to our everyday lives. We know too much about the facts to be satisfied with theories based on simple abstractions and too little to trace the guiding clues through their manifold complexities or to handle simultaneously the many variables that must be considered. From the point of view of a lecturer to a general audience, therefore, the subject I wish to discuss tonight is in a very unsatisfactory state. My problem has been to distill from the mass of material available some thoughts on the subject that might be condensed into the space of one lecture and still be of interest to you.

THE HISTORICAL APPROACH TO COMPLICATED PROBLEMS

In the first verse of the fifty-first chapter of the Book of Isaiah, you will find the words "Hearken to me, ye that follow after righteousness, ye that seek the Lord: look unto the rock *whence* ye are hewn, and to the hole of the pit *whence* ye are digged." I have always been fascinated by this passage in which Isaiah exhorts us to make or renew the acquaintance of our intellectual ancestry, to seek an understanding of things as they are from a deeper knowledge of how they came to be so, and I think that we may apply this thought with profit to such a complex problem as the theory of solutions.

I wish, however, to digress a moment and call your attention to some thoughts of a general nature that are suggested by Isaiah's exhortation. It is quite certain that even in their wildest dreams neither the prophet nor his hearers ever imagined that men could spend their lives in the pursuit of what we call Science, and yet his words and the very figures of speech employed are so happy in their application to natural philosophers that I would advocate their inscription on the walls of all places where scientific research is fostered. Consider the phrase "look to the rock whence ye are hewn." Does it not imply a high degree of permanence in the system of which we are a part? Does it not imply an association in something much more fundamental and lasting than ourselves? It is interesting to compare this thought with that expressed by Wordsworth and familiar to all readers of "Nature":

> To the solid ground
> Of Nature trusts the mind that builds for aye.

We have assurance that this is not just poetic fancy from the researches of one of the greatest scholars in the history of science, for George Sarton has stated as his considered opinion that "scientific activity is the only human activity that is obviously and undoubtedly cumulative and progressive."[2] To continue the metaphor, each chip hewn from the rock is a step toward the final statue. We see the image more clearly and hew our chips more intelligently because of the work done by our ancestors. In other words, scientific progress is the one thing we can bequeath to posterity that will not be nibbled at by inheritance taxes on personal reputations, annihilated by the inflations or deflations of fluctuating fashions and taste, or squandered by carelessness or indifference.

Dignified as the metaphor of the rock may be, the exhortation to "look to the pit whence ye are digged" is even more appealing to

[2] SARTON, G. *The history of science and the new humanism*, p. 24. New York, 1931.

chemists and biologists and others who work in the messier regions of science. The metaphor implies a humble origin, an intimate contact with the soil of life, a certain amount of monotonous drudgery, a painful groping and digging in an a most boundless quarry for something we do not even know to be there, a laborious sifting of the gold from the dross. It also carries a warning that even when the nugget of truth is found, it will be contaminated with the dirt of irrelevancy or error.

The broadened outlook on scientific problems that comes to many of us most easily through a background of historical knowledge, through looking into "the pit whence we are digged," is so valuable that I think at least one member of each of the scientific departments of our large graduate schools should be versed in this aspect of his subject. I do not advocate that the memories of graduate students already burdened with a heavy technical load should be made to carry an extra weight of names and dates, but that there should be someone to stimulate them to ask: Where did this idea come from, how did this theory arise? Habits of thought so stimulated can make several significant contributions to the intellectual equipment of research workers. In the first place, even a moderate familiarity with the historical development of our own or cognate fields enables us to put ourselves into the frame of mind of the masters who made the great advances in the past. If we take the trouble to understand their background, the problems as they saw them, the ideas available to them and the sources of these ideas, we can trace their steps through the arguments leading to important conclusions and try to emulate them. Glimpses of the turning points where they hesitated and the reasons that led them to prefer one road to the others are probably more valuable to the research student than the great discoveries themselves that now form an integral part of recorded science.

Secondly, I think we can gain the confidence that comes from a perspective of our subject, a perspective that enables us to differentiate between apparent difficulties that arise from elaboration of simple principles and real difficulties that arise from lack of principles or absence of a trustworthy logic for handling simultaneously the numerous variables of a complicated problem. An interesting result of even a superficial study of this sort is the realization that the intrinsically mysterious parts of physics, chemistry, or biology are not the theories but the phenomena presented by nature and observed by experiment. What the mind of one man can invent, that of another can grasp, granted that the proper effort is made and that the theory is not purely fantastic; but we must still agree with Hamlet that "there

Ralph E. Gibson, retiring president of the Philosophical Society of Washington

are more things in heaven and earth than are dreamed of in our philosophy." The basic ideas, the concepts, and the hypotheses on which the theories of physics and chemistry are based were drawn originally from every-day experience and are very limited in number; for example, pushing with a stick (waves) and throwing stones (particles) are the only mechanisms we can imagine for action at a distance. As a science develops, the concepts and hypotheses are refined and modified in the light of the new specialized experience, with the result that the very foundations of a theory become somewhat removed from every-day experience, and the beginner is confronted with difficulties that are not lessened by the limitations of our vocabulary. An excursion into the past leading to a knowledge of where these ideas came from and how they grew helps greatly in removing these obstacles.

An unnecessary source of difficulty in the theoretical phases of science is the natural and, in some ways, laudable passion for elegance on the part of some thinkers. In constructing their theories these men start from current ideas, explore and reject many possibilities, and frequently achieve success by an inspired guess which is justified *a posteriori* by rigorous means. When their theory is finished, they proceed to polish it, to obliterate the traces of fumbling, to revise and refine the basic ideas and, in short, they end by presenting a picture that is most satisfying to one who is already familiar with the result but that is baffling to the unsophisticated. The nugget of truth is so carefully polished that all traces of the pit are removed. One can not condemn this desire, but one can deplore the loss of those revealing intermediate steps that might have meant so much to the neophyte. I am convinced that the difficulty that most chemists and many physicists encounter in learning mathematics arises from this source. The subject has been worked over by many generations of mathematicians who have not only polished out the marks of the chisel but have also surrounded the rock with the cloud of generality and covered it with the moss of rigor.

In the light of a historical survey, we may also see that many of the controversies between seemingly rival theories arose largely from the fact that the antagonists, working on different aspects of the same complex problem, derived their basic ideas from different backgrounds of experience. I shall illustrate this later by the so-called physical and chemical theories of solutions. Human limitations have forced us to split up the study of nature into different fields. While organizers, administrators, and others who can not function without labels have

made the most of this classification, it is one which the true natural philosopher will never cease to fight. The history of science is full of examples of great advances that came from the transfer of ideas from one field to another: Kekulé advanced organic chemistry because he had been an architect; Faraday made some of his greatest contributions to physics because he was also a chemist. Frequently a satisfactory theory of complex phenomena can be developed only when concepts and hypotheses from several of the arbitrary divisions of science are combined.

ORIGIN AND DEVELOPMENT OF SOME IDEAS USED IN THE THEORY OF SOLUTIONS

In asking you now to accompany me in taking a few fleeting glances into the pit whence our modern theories of solutions have been digged, I want first to indicate one general conclusion for your guidance. We shall see that the subject is not so narrow as might appear at first sight, because, in their attempts to understand the highly complex problems presented by solutions, investigators have pressed into their service all the physical and chemical ideas available to them in their age. Consequently, the story of the development of the theory of solutions is a mirror in which we see reflected the advances in physical and chemical thought of all the ages, and I have borrowed this figure of speech with modifications from P. Walden[3] to serve as the title of this address.

Early Physical Theories

Somewhat arbitrarily, I shall begin this story in the first half of the seventeenth century A.D., not because the speculations made prior to that time lacked interest—in some ways they are the most interesting part of the subject—but because this period marks the beginning of a radical departure from the use of purely anthropomorphic ideas to the introduction of ideas culled from analyzed experience by students of the infant science of physics and the embryo science of chemistry. Up to this time the phenomena of solubility, especially of solids, had been explained in terms of the Doctrine of Affinity or the attraction of closely related materials. A liquid dissolved a solid because something in the solid was closely related to the liquid and wanted to be with it. The introduction of new ideas may be illustrated by a quotation from Robert Boyle[4] written in 1663 which sums up one advanced school of thought at that period:

[3] WALDEN, P. *Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge*, p. 3. Stuttgart, 1910.

[4] BOYLE, R. Essay entitled "Of the Producibleness of Chymical Principles" (1663). See *The Works of Robert Boyle*, London, 1772.

These two objections I thought fit to couch together, to be able, in fewer words, to answer them both: I considered then, that amalgamation being, in effect, but a kind of dissolution of metals in a menstrum or fluid body (for such mercury is, in reference to them), there is no necessity, that the solvent should find in the metal a copious ingredient just of its own nature; for dissolution depends not so much upon the pretended cognation between the solvent and the body it is to work on, as upon congruity, as to size and figure, between the pores of the latter and the corpuscles of the former.

Sixteen years earlier, Pierre Gassendi[5] (1592–1655) had given a similar atomistic theory of solutions. He held that all matter was made up of atoms or molecules that had characteristic sizes, shapes, and weights. When these atoms were packed together to give a solid or liquid, small interstices or pores remained, and when a salt dissolved in water it merely occupied the pores in the water, the solution becoming saturated when all the pores were filled. The shapes of the corpuscles of matter were inferred from their crystalline forms; thus common salt had cubic corpuscles, and this argued the presence of cubic pores in water; alum had octahedral corpuscles, and it was concluded that there were octahedral pores in the water. Lack of solubility indicated the absence of pores of the proper shape.

The French philosopher N. Lemery[6] also developed ideas of the same type. By the middle of the seventeenth century, therefore, physicists were using ideas about the nature of solutions that are current today, the corpuscular nature of matter and the geometrical ideas of packing. The atomic nature of matter was firmly embedded in their thinking, a fact that is not surprising in view of the material available. In their speculations about matter they had two, and only two, alternatives based on analogy with every-day experience to choose from. Either matter resembled a liquid, such as water, and was continuous, i.e., divisible without any limit, or it resembled a heap of unbreakable stones, i.e., was atomic in nature. Those philosophers who studied the phenomena of solutions could not bring themselves to believe that two continuous bodies, such as salt and water, could intermingle with such ease, and for this and other cogent reasons they had to reject the continuous theory of matter and adopt the only other possible choice. With the rock-pile hypothesis, the interstices or pores must, of course, go, and the step from this to geometrical relationships and the packing together of bodies is a short one. The hypothesis of pores or voids in liquids was strengthened somewhat later by the observations of Bishop Watson[7] and of Reaumur[8] that a contraction occurred when

[5] GASSENDI, PIERRE. *Opera Florentiae*, 1684. See MELLOR, J. W. *A Comprehensive treatise on inorganic and theoretical chemistry*, vol. 1, p. 574, London, 1922.
[6] LEMERY, N. *Cours de chymie*, Leyden, 1716. See WALDEN, *op. cit.*, p. 25.
[7] WATSON, R. Phil. Trans. 59: 325, 354. 1770.
[8] REAUMUR. See WALDEN, *op. cit.*, p. 28.

many pairs of liquids were mixed. These we might call the physical or mechanical theories of the Age of Boyle.

Early Chemical Theories

There were other notable investigators who even in the eighteenth century rejected this purely mechanical picture of the phenomenon of solution and held that solution represented a union between the solvent and the solute (F. Hoffmann, 1722), or implied a definite relationship (affinity) and similarity between the solvent and the dissolved substance (Stahl). Still another worker (Digby, 1603–1665) suggested that when a salt dissolves in water, each particle of salt incorporates with itself at least one particle of water, an intimate union suggestive of the hydrate theories that are still used.

These were chemical theories of the Age of Boyle and are mentioned here chiefly to introduce the rivalry between the so-called chemical and mechanical or physical theories of solutions that has persisted almost to this day.

Physical Theories of the Eighteenth Century—Influence of Newton

At the beginning of the eighteenth century, new ideas were introduced into the theory of solutions that reflected the tremendous advances in physics that marked the preceding 25 years. Newton's studies in optics, particularly of the phenomena of refraction and double refraction, led him to speculate on the nature of the interaction of light and matter and, incidentally, the nature of matter in general and of solutions in particular. I quote the following passages from Part I, Book 3, of Newton's *Opticks*, published in 1704.[9]

Quest. 31. Have not the small Particles of Bodies certain Powers, Virtues or Forces, by which they act at a distance, not only upon the Rays of Light for reflecting, refracting, and inflecting them, but also upon one another for producing a great Part of the Phænomena of Nature? For it's well known, that Bodies act one upon another by the Attractions of Gravity, Magnetism, and Electricity; and these instances shew the Tenor and Course of Nature, and make it not improbable but that there may be more attractive Powers than these. For Nature is very consonant and conformable to herself. How these Attractions may be perform'd, I do not here consider. What I call Attraction may be perform'd by impulse, or by some other means unknown to me. I use that Word here to signify only in general any Force by which Bodies tend towards one another, whatsoever be the Cause. For we must learn from the Phænomena of Nature what Bodies attract one another, and what are the Laws and Properties of the Attraction, before we enquire the Cause by which the Attraction is perform'd. The Attractions of Gravity, Magnetism, and Electricity, reach to very sensible distances, and so have been observed by vulgar Eyes, and there may be others which reach to so small distances as hitherto escape Observation; and perhaps electrical Attraction may reach to such small distances, even without being excited by Friction.

[9] NEWTON, ISAAC. *Opticks*. Reprinted from ed. 4 (William Innys, London, 1730), pp. 375, 387. G. Bell and Sons, Ltd., London, 1931.

For when Salt of Tartar runs *per Deliquium*, is not this done by an Attraction between the Particles of the Salt of Tartar, and the Particles of the Water which float in the Air in the form of Vapours? And why does not common Salt, or Salt-petre, or Vitriol, run *per Deliquium*, but for want of such an Attraction? Or why does not Salt of Tartar draw more Water out of the Air than in a certain Proportion to its quantity, but for want of an attractive Force after it is satiated with Water? And whence is it but from this attractive Power that Water which alone distils with a gentle luke-warm Heat, will not distil from Salt of Tartar without a great Heat? And is it not from the like attractive Power between the Particles of Oil of Vitriol and the Particles of Water, that Oil of Vitriol draws to it a good quantity of Water out of the Air, and after it is satiated draws no more, and in Distillation lets go the Water very difficultly? And when Water and Oil of Vitriol poured successively into the same Vessel grow very hot in the mixing, does not this Heat argue a great Motion in the Parts of the Liquors? And does not this Motion argue, that the Parts of the two Liquors in mixing coalesce with Violence, and by consequence rush towards one another with an accelerated Motion? . . .

If a very small quantity of any Salt or Vitriol be dissolved in a great quantity of Water, the Particles of the Salt or Vitriol will not sink to the bottom, though they be heavier in Specie than the Water, but will evenly diffuse themselves into all the water, so as to make it as saline at the top as at the bottom. And does not this imply that the Parts of the Salt or Vitriol recede from one another, and endeavour to expand themselves, and get as far asunder as the quantity of Water in which they float, will allow? And does not this Endeavour imply that they have a repulsive Force by which they attract the Water more strongly than they do one another? For as all things ascend in Water which are less attracted than Water, by the gravitating Power of the Earth; so all the Particles of Salt which float in Water, and are less attracted than Water by any one Particle of Salt, must recede from that Particle, and give way to the more attracted Water.

When any saline Liquor is evaporated to a Cuticle and let cool, the Salt concretes in regular Figures; which argues, that the Particles of the Salt before they concreted, floated in the Liquor at equal distances in rank and file, and by consequence that they acted upon one another by some Power which at equal distances is equal, at unequal distances unequal. For by such a Power they will range themselves uniformly, and without it they will float irregularly, and come together as irregularly. And since the Particles of Island-Crystal act all the same way upon the Rays of Light for causing the unusual Refraction, may it not be supposed that in the Formation of this Crystal, the Particles not only ranged themselves in rank and file for concreting in regular Figures, but also by some kind of polar Virtue turned their homogeneal Sides the same way.

The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked Atoms, which is begging the Question; and others tell us that Bodies are glued together by rest, that is, by an occult Quality, or rather by nothing; and others, that they stick together by conspiring Motions, that is, by relative rest amongst themselves. I had rather infer from their Cohesion, that their Particles attract one another by some Force, which in immediate Contact is exceeding strong, at small distances performs the chymical Operations above-mention'd, and reaches not far from the Particles with any sensible Effect.

These quotations show quite clearly, I think, that the Atomic Theory of matter was firmly fixed in Newton's mind and that he saw in chemical phenomena, including solutions, an application of the same ideas that he had used so successfully in describing the motion of

heavenly bodies. We see here the introduction of the idea of forces between atoms or molecules, forces which *varied with the distance* and not only compelled them to attract or repel each other but to influence light. This was really a great advance over the older ideas that chemical interaction resulted from the desire of like bodies to be together. We see also the evolution of a specific nature in these forces, together with ideas of saturation. It is also interesting to note that Newton had a clear picture of the relationship of heat to molecular motion and the use of thermal measurements for estimating the magnitude of the forces holding the corpuscles of matter together, although nearly 150 years were to elapse before the kinetic theory of heat became firmly established.

Although Newton is purposely and cautiously vague about the nature of the forces between atoms, he did extrapolate his gravitational theory far enough to say one thing about these forces and make thereby a most important advance over the current ideas. He does imply that these intercorpuscular forces are functions only of the distance between the particles, "by some Power which at equal distances is equal and at unequal distances unequal," and he shows that regularity in the spatial arrangement of the particles of solid bodies follows from such a law. He goes even farther, and from his observation on the double refraction of crystals of calcite he arrives at the idea of orientation of the ultimate particles of calcite that arise from a "polar virtue" of those molecules, i.e., a property whereby the forces acting on one part of the molecule are different from those acting on the other.

In some form or other, these ideas of Newton are in use today, and I have spoken of them in some detail, not for the purpose of showing that Newton foreshadowed many modern theories of solution but to show how a powerful mind took ideas from his analyzed experience in the study of the motions of heavenly bodies and the properties of light, extracted some of the *essentials* and applied them in an entirely different field with results that still excite our interest and admiration.

These ideas of Newton were slowly absorbed during the eighteenth century and were reiterated and developed by the French naturalist Buffon (1707–1785),[10] who wrote, "The laws of affinity are the same as the general law which governs the interaction of the heavenly bodies, the specific attractions (attractions particulières) are due solely to the shapes (figures) of the molecules because these shapes enter as an element in the distance between them." He goes on to show how the shapes of the bodies are unimportant in astronomy but may be very

[10] See WALDEN, *op. cit.*, p. 37.

significant in determining interactions in bodies as close together as molecules.

The end of the eighteenth century also saw a definite realization among philosophers that the phenomena of solubility, of the density of bodies, their adhesion, cohesion, and chemical affinity, all were related through a single unifying principle, the attractive forces between the units of matter. There were still, however, two main schools of thought, the *physical school* and the *chemical school.* The former based their theories on ideas such as those I have just outlined, the latter insisted that a solution represented a chemical combination between the solvent and the dissolved substance. This school (Wallerius, Klaproth, and others) held that the cohesion and adhesion of matter also was a chemical phenomenon and that solutions depended on the balance of the adhesive (unlike molecules) and cohesive (like molecules) affinities. It is evident that the difference between the physical and chemical theories depended mostly on the background of the thinker, whether he chose his fundamental ideas from physics, the attraction, shape, pores, or geometry of large bodies, or whether he chose his ideas from experience in the violent combinations known as chemical reactions.

An important clarification of thought concerning solutions was made by Lavoisier toward the end of the eighteenth century when he distinguished between solution and dissolution. Solution he reserved for reversible phenomena, such as the dissolving of salt in water, when the salt is recovered by simple evaporation. He applied the term dissolution to cases such as the dissolving of a metal in an acid where the metal is not recovered on evaporation, but instead of it a salt. In this case a definite chemical change accompanied the process of solution.

The Early Nineteenth Century—Chemical Theories

The beginning of the nineteenth century saw the introduction of the atomic theory of matter into experimental chemistry through the law of definite proportions, the law of multiple proportions, and the law of reciprocal proportions. From these empirical laws, the chemists Dalton, Richter, and Berzelius established a quantum theory of chemically reacting masses that sharpened the definition of a chemical compound and soon increased the embarrassment of those who held the view that solutions were purely manifestations of chemical combination. Some, however, like C. L. Berthollet, never accepted the laws of definite and multiple proportions and could therefore consistently retain such opinions. Others, in spite of an acceptance of

Dalton's theory, continued to believe that the dissolved substance and the solvent were chemically combined. An excellent summary of the chemical theory of solutions from 1800 to 1880 is given by W. A. Tilden,[11] who quotes a statement by Josiah P. Cooke written in this country in 1881 that "the facts seem to justify the opinion that solution is in every case a chemical combination of substances dissolved with the solvent, and that it differs from other examples of chemical change only in the weakness of the combining force."

Time does not permit me to elaborate further on these chemical theories; I have felt that some discussion of them is necessary in order to balance the picture, but we must return to the main subject and see how the advances in physics during the nineteenth century are reflected in the theories of solutions. We shall see later the ultimate fate of the controversy between chemical theories and physical theories.

Electrical Theories

By the year 1800 sources of voltaic electricity had been developed and the fundamental laws governing the attraction and repulsion of electrostatic charges had been established by the physicists. Chemical effects of electrical currents also were being investigated. It is not surprising, therefore, that electrical ideas were incorporated into chemical thought at this time. We are all familiar with the extensive theory in which Berzelius attempted to explain all chemical combination by the action of forces between electrical charges, an attempt that failed because chemists of that time knew too much about chemistry and the physicists too little about electricity. Some years before Berzelius's theory, Th. von Grotthuss applied electrical ideas to solutions, particularly those that conducted electricity. He considered water as a dipole, the hydrogen being associated with positive electricity and the oxygen with negative electricity, and assumed that a continuous dissociation and recombination of these dipoles took place so that there was a constant interchange of partners among the water dipoles. In the same way an electrolyte, such as a salt, was supposed to be composed of a positive and a negative part (e.g., Na^+ and Cl^-) and it was thought that a constant exchange of partners among the dissolved molecules also occurred. All this happened without the passage of electric current through the solution, but, as we should say today, the exchange of partners was purely random. When positive and negative electrodes were placed in the solution, a direction was given to this exchange with the result that current flowed and electrolysis took place.

[11] TILDEN, W. A. British Assoc. Reports, 1886, p. 444.

Of especial interest is the picture that Grotthuss gave of the solubility of electrolytes, e.g., salts. He suggested that the solubility of such substances depended on their capacity to split up their "polar-electric elementary particles," i.e., ions, and in the association of these ions with the molecular galvanic activity of the water. The work of Grotthuss marks the introduction of ideas drawn from electrical observations to give a mechanism for the vague ideas of chemical affinity, and he suggests that the solubility of salts in water is an electrochemical phenomenon depending on the interaction between the water molecules acting as electrical units and the ions into which the dissolved electrolytes resolve themselves.

The Kinetic Theory

The next important set of ideas that we find introduced into the theory of solutions reflects an advance in physics for which the nineteenth century will always be famous in the annals of science. I refer to the establishment of the kinetic theory of heat and matter on a firm experimental and logical basis by Clausius and others.

Members of both the physical and chemical schools of thought in the early nineteenth century seem to have had a clear recognition of the relations between those forces that caused one substance to dissolve in another and those forces that gave rise to cohesion in solids and liquids. For example, the French chemist Dumas[12] wrote in 1836, "Molecular attraction manifests itself in three well differentiated ways, between molecules of one and the same body, this is the ordinary cohesion of the physicists, between more or less similar molecules, which mix in such a way as to preserve their individual properties—that is the force of solution, and finally between dissimilar molecules which unite intimately giving a product of quite different properties—this is Affinity." Such views were generally held and attempts were made to explain the solubility of solids and especially saturated solutions in terms of competing forces—forces between the solvent and solute molecules producing solution on the one hand and forces of cohesion opposing the dispersion of the solid on the other. These investigators apparently felt the need of a *general type of force or agency opposing cohesion*, an agency that tended to separate molecules from each other. Newton supplied this need by repulsive forces, but it is just as well that his ideas on this subject did not spread, although it is to be regretted that no one followed up his ideas of heat as a measure of molecular attraction.

[12] DUMAS, J. B. A. *Leçons sur la philosophie chimique*, ed. 1, p. 391. Paris, 1837.

When the theory that heat is a form of molecular motion was firmly established on an experimental basis, this general dispersing agency was at once apparent in the kinetic energy of the molecules. For example, Clausius and Joule showed that the pressure of a gas was entirely due to the motion of the molecules, and the processes of melting, evaporation, and sublimation were at once thought of as taking place when the temperature and hence the kinetic energy of the molecules became large enough to overcome the forces of cohesion.

From 1860 to 1885, therefore, a number of theories, e.g., those of L. Dossios (1867), W. W. J. Nicol (1883), Gay-Lussac, and W. A. Tilden and W. A. Shenstone (1884) appeared in which the kinetic energy of the molecules played an important role in the discussion of solubility and other phenomena connected with solutions. For example, Tilden and Shenstone examined the connection between the solubility and the fusibility (melting point) of salts showing in general that the lower the melting point, the more soluble was the salt, and wrote:[12]

> But the connexion between fusibility and solubility, though proved does not wholly explain the nature of the initial stage in the process of solution of a solid. It does, however, strongly support a kinetic theory of solution based on the mechanical theory of heat. The solution of a solid in a liquid would accordingly be analogous to the sublimation of such a solid into a gas, and proceeds from the admixture of molecules detached from the solid with those of the surrounding liquid. Such a process is promoted by rise in temperature, partly because the molecules of the still solid substance make larger excursions from their normal centre, partly because they are subjected to more violent encounter with the moving molecules of the liquid. Such a view does not necessarily involve the assumption of an "attraction" between the molecules of the solvent and those of the solvend (Cf. L. Dossius, Jahresb. (1867), 92. Nicol, Phil. Mag. Feb. 1883).
>
> Indeed it is difficult to disconnect "attraction" from the idea of combination resulting from such attraction. In some cases we are considering, e.g. the solution of anhydrous Na_2SO_4 in water at 100°, nothing like combination between water and salt seems to occur.

We notice that the role of the attractive forces between molecules in solutions, introduced by Newton, is being abandoned and attempts are being made to explain all the phenomena by the kinetic theory.

The Kinetic Theory of Van't Hoff

These theories were, however, completely overshadowed by the kinetic theory picture developed a year or so later (1887) by van't Hoff from a study of the osmotic pressure of solutions. It had been known for a long time that, if a solution were placed in a strong vessel and connected with the pure solvent by a membrane permeable to the solvent, but not to the dissolved substance, solvent flowed through

[12] TILDEN, W. A., and SHENSTONE, W. A. Phil. Trans. Roy. Soc. **175A**: 30. 1884.

the membrane into the solution until a definite pressure was developed in the vessel containing the solution. This pressure was called the Osmotic Pressure. Van't Hoff showed from the experimental results of Pfeffer that the following relationship held in dilute solutions: $\pi = (n/V)RT$ where π is the observed osmotic pressure, n is the number of gram molecules dissolved in a volume V, T is the absolute temperature, and the constant R has the same value as the well-known gas constant. The analogy of this result with the equation of state for an ideal gas $P = RT/V$ led van't Hoff to regard the dissolved substance as an ideal gas dispersed in a solvent whose role was that of a modified empty space and, of course, to treat the osmotic pressure as the pressure of an ideal gas, i.e., of purely kinetic origin. This theory was brilliant and led to some excellent experimental work, notably that of H. N. Morse and his students in Baltimore, who showed that the law was limited to very dilute solutions, if exact application were desired, and who studied the effects of temperature and the nature of the solvents and dissolved substances. The theory suffered from the fate common to all simple theories in this field, it long outlived its usefulness. You will notice that the theory exalts one idea, namely, the kinetic energy of the dissolved substance, to a position that excludes all the other considerations we have spoken of. Such a defect is fatal in so complicated a subject. The result was that several generations of chemists had to learn all about the osmotic pressure of solutions under the impression that it was a unique and fundamental quantity, and they tried to patch up the theory of van't Hoff to cover regions where, by its fundamental assumptions, it was inapplicable. Like too many theories, that of van't Hoff started as a strong current carrying the ship of science into broader waters of knowledge and ended up by being a whirlpool in which there was plenty of motion but all in a circle.

Thermodynamics—Entropy and Energy

The decade from 1880 to 1890 saw the beginning of a series of extensive and intensive researches on the properties of solutions which has continued unabated to this day. Indeed, these studies have constituted a major part of the science of physical chemistry that dates from 1887, the year of the publication of the first volume of the Zeitschrift für Physikalische Chemie. In order to understand this activity, we must recall that by 1880 chemistry was on a sound basis. Not only was the atomic theory firmly established but definite and trustworthy ideas about molecules had also been developed and a consistent system of molecular and atomic weights was available. Hypotheses of

valency or the combining powers of the elements had been tested experimentally and a convenient, simple, and consistent scheme had been devised for the formulation of elements and compounds. At this time, too, we see a new reflection appearing in our mirror, a reflection that was to become a floodlight revealing relations among many apparently disconnected phenomena. I refer to the science of thermodynamics. Although thermodynamics and the kinetic theory were "nursed upon the selfsame hill," they are different in character. Classical thermodynamics is now a self-contained science based on two fundamental laws whose validity has been placed beyond doubt by experiment. From these two laws, deductions reaching into all branches of science have been made by unimpeachable mathematics. The science deals with experimental quantities, heat, work, temperature, pressure, and functions formally derived from them, and its theorems are exact. It is one of the few branches of physics that have come unscathed through the recent revolutions. The reason is that thermodynamic arguments depend only on observables and are independent of any hypothesis concerning the nature of matter.

The function of thermodynamics in physical chemistry has been to provide exact relations among observable quantities, thereby promoting economy, not only of measurement by limiting the number of experiments we have to do, but also of thought by allowing us to pass readily and exactly from measured quantities whose theoretical significance is obscure to those whose interpretation is more readily seen. In other words, thermodynamics gives us an exact system into which the experimental results of physical chemistry in general and the studies of solutions in particular, may be fitted, a system which enables us to examine the results from many points of view and pass to the more abstract quantities, such as energy and entropy, which lead directly into the kinetic theory and statistical mechanics.

Because of its very nature it was not to be expected that thermodynamics could supply any new mechanisms for use in the theory of solutions, but this science did make an important contribution to the theory in that imperceptibly but inexorably it forced physical chemists to think simultaneously of several variables, the forces between molecules, their geometry, and their kinetic energy. This came about because the thermodynamic criterion of equilibrium insists that we consider at the same time both energy and entropy, potential energy (forces), and kinetic energy (motion). I shall illustrate this by an example drawn from ideal solutions where changes of energy are zero.

Suppose I have two liquids A and B, such that the forces between

the molecules A and A, B and B, and A and B are the same, and I place A and B in contact. I shall find that at constant temperature, a spontaneous process takes place and that finally I get a homogeneous solution AB. If the liquids are properly chosen, careful measurements will also show that there is no heat and no volume change during the process, but in spite of this we know that the final state is definitely different from the initial state, and we want to find the physical quantity that reflects this change. Thermodynamics provides such a quantity in the *entropy* of the system and furthermore says that, since the change was a spontaneous one, the change in entropy is *greater* than the heat absorbed divided by the absolute temperature, i.e., greater than zero in this case. Hence the entropy *increased* during this process.

With the aid of the kinetic theory or elementary statistical mechanics, we can go farther and see that the entropy of a substance may be measured by the volume in configuration space that the coordinates of its molecules may occupy, together with the volume in momentum space that the points representing the momenta of its molecules and their moving parts may occupy. At constant temperature, we may consider that this latter part of the entropy is fixed and conclude that the increase of entropy that accompanied the mixing of liquids A and B arose solely from the fact that the molecules of each found larger volumes available to them. Indeed, from elementary statistical mechanics, we may see that the following expressions represent what happened:[14]

$$S_A - S_A^0 = -R\ln X_A \qquad (1)$$

$$S_B - S_B^0 = -R\ln X_B. \qquad (2)$$

Let us carry the argument one step farther and change the temperature so that one of our pure liquids freezes—we shall then be dealing with the solubility of a solid in a liquid; naphthalene in contact with benzene is an actual example that approximates to the conditions I am describing When the solution is saturated, we have coexisting at equilibrium solid A (naphthalene) and a solution of A and B. Under such conditions, thermodynamics tells us that the pressure and the temperature must be the same in both phases and that the following relation must hold for the component that is present in both phases, the naphthalene in this example:

[14] In this example the symbols have the following meaning: S_A is the partial molal entropy of substance A in the solution, S_A^0 is the molal entropy of pure liquid A, S_A^S is the molal entropy of solid A, X_A is the mole fraction of A in the solution. S_B, S_B^0, S_B^S and X_B are the same quantities for component B. H_A, H_A^0, H_A^S are the molal heat contents corresponding to these entropies (the heat content is the total energy + the pressure multiplied by the volume). R is the conventional gas constant per gram molecule. T is the absolute temperature.

$$H_A^S - TS_A^S = H_A - TS_A \tag{3}$$

i.e.,

$$H_A - H_A^S = T(S_A - S_A^S). \tag{4}$$

and, if there is no heat change when the liquids are mixed,

$$H_A^0 - H_A^S = T(S_A - S_A^S) \tag{5}$$

where $(H_A^0 - H_A^S)$ is the ordinary heat of melting of the solid A, which may change with temperature but this change depends only on substance A and not on the solution. With the help of equation (1), we may go farther and write

$$\frac{(H_A^0 - H_A^S)}{T} = (S_A^0 - S_A^S) - R\ln X_A. \tag{6}$$

This picture gives a direct connection between solubility and melting in the ideal case. At the melting temperature of A, i.e., $T = T_m$, we know that $(H_A^0 - H_A^S) = T_m(S_A^0 - S_A^S)$ or $X_A = 1$, i.e., pure liquid A is in equilibrium with solid A.

Since solids freeze spontaneously below their melting points, we see that $(H_A^0 - H_A^S)/T$ is greater than $(S_A^0 - S_A^S)$ if T is less than T_m, in which case the equation is balanced only if $R\ln X_A$ is negative or X_A is between 0 and 1, a positive fraction representing the solubility of solid A in liquid B.

This example shows (1) that the solubility of solid A is due to the increased entropy that A gets when its molecules are dispersed in B (indeed, the term $-R\ln X_A$ actually measures this entropy change) and (2) that this solubility will increase with temperature, a well-known experimental fact.

This is the thermodynamic description of the state of affairs in an ideal solution and is the basis of a general theory of solutions today. Wherein does this differ from the theory of van't Hoff or other kinetic theories; are we still regarding the dissolved substance as an ideal gas in an inert medium? The answer is interesting. So far as the entropy change on mixing is concerned, we are considering the dissolved substance as an ideal gas, but as regards energy changes we are assuming that a molecule of A is acted on by the same forces when immersed in liquid B as when it is surrounded by molecules of its own kind. It is certainly not a gas from this point of view. The interactions between molecules A and A, B and B, and A and B are, therefore, of great importance, and only in very rare cases is an ideal solution, as pictured above, realized experimentally. Generally speaking, the solubility of A in B will be greater than the ideal solubility given by a calculation analogous to that just described if the A–B attractive forces are

greater than the A – A or B – B forces, and less if the opposite conditions hold. One of the chief lines of attack on the problem of solutions today is directed toward finding out the nature of intermolecular forces between like and between unlike molecules and applying this knowledge through statistical mechanics to obtain an adequate quantitative description of the properties of solutions as observed in the laboratory.[15] It should be mentioned that the intermolecular forces and the geometry of the systems not only influence the energy but also add to the entropy terms that must be considered along with the ideal entropy of mixing. In recent years some instructive attempts to calculate the energy and the entropy of solutions have been made.[16]

The point we have now reached in our consideration of the evolution of the ideas used in the theories of solutions is well into the twentieth century. Let us pause to gather together some of the ideas of which I have spoken. The list is by no means exhaustive, but it contains most of the raw material of which modern theories are made: (1) *Corpuscular nature of matter* (older philosophers); (2) *geometry of corpuscles or molecules*—size, shape, packing, voids or holes in packing (Boyle, Gassendi); (3) *general forces* between molecules—attraction and repulsion (Newton, Buffon—developments of mechanics); forces that are functions of distance only; (4) *orientation of corpuscles*—light as means of investigating matter (Newton); (5) *chemical theories*—specific but unknown chemical forces as opposed to general physical forces causing attraction or cohesion of molecules; connection between forces producing cohesion and forces producing solution; (6) *electrical nature of forces* causing chemical combination, cohesion, and solution—electricity in molecular systems (Grotthuss, Berzelius); (7) *kinetic theory of matter*—heat as form of molecular motion; disordering effect of heat and temperature; gas picture of solutions; relation of solubility and melting; (8) *thermodynamics*—unification of experimental results; quantitative studies of equilibrium and direction of physicochemical changes; heat *and* entropy; (9) *statistical mechanics.*

[15] Although by far the greater portion of the effort devoted to the study of solutions has been directed toward the problem of solutions of electrolytes in water and developments of great importance have been made in this field, limitations of space prevent the discussion of theories of electrolytes here. It has been realized for many years that strong electrolytes exist mostly as positively and negatively charged ions in water solutions, and since the potential fields around ions are well known, the application of elementary electrostatics and statistical mechanics has led to noteworthy advances in the understanding of the subject. Electrolytes form a case where an important part of the intermolecular action (forces between the ions) is known. A general formulation of solution theory into which the treatment of electrolytes or non-electrolytes may be fitted is given by J. G. KIRKWOOD (Chem. Rev. 19: 275. 1936).

[16] BERNAL, J. D., and FOWLER, R. H. Journ. Chem. Physics 1: 515. 1933; ELEY, D. D., and EVANS, M. G. Trans. Faraday Soc. 34: 1093. 1938; EVERETT, D. H., and COULSON, C. A. Trans. Faraday Soc. 36: 633. 1940.

RECENT DEVELOPMENTS

The next part of my story concerns the further development and refinement of these ideas, but now a change takes place in our perspective. We have been seeing various advances in physics reflected in the mirror of the chemistry of solutions, but now our mirror becomes transparent and we look through the phenomena of chemistry into the realm of physics that underlies them and find that the interface that separated these sciences was not real but was placed there by the limitations of our own point of view. Those unknown attractive forces about which Newton speculated, the same unknown forces that caused the disputes between those who supported the chemical theories and those who supported the physical theories, are becoming known, and in the light of this knowledge the boundary between physics and chemistry is fading. The faint reflection that Grotthuss and Berzelius caught has grown to the magnitude of a sun, and to its light we owe our present knowledge.

Even an outline of how this change has come about would take several lectures, and it is a subject with which most of you are familiar, anyway. I shall, therefore, merely mention a few landmarks.

Through the experimental researches of Faraday and the work of the brilliant theoretical physicists of the second half of the nineteenth century, notably Maxwell, the sciences of electromagnetics and electrostatics rose to their full stature. The researches of J. J. Thomson and his school, together with the discovery of radioactivity, established on an experimental basis the corpuscular nature of electricity and the electrical nature of matter. The researches of the spectroscopists, together with the inspiration of Bohr and his followers, when added to these results, have led to the universal acceptance of the theory that the atoms of matter are complex systems composed of elementary electrical particles, electrons, protons, positrons, etc. Finally, the development of quantum mechanics removed the last obstacle that stood in the way of a general conclusion that in principle all forces of attraction and repulsion between atoms and molecules arise from the complex electrostatic interactions of the charges of which they are composed. Thus those forces producing chemical combination, physical cohesion, the solubility of one substance in another, and all the other metamorphoses observed in nature are believed to be the result of a complex system of positive and negative electrical charges seeking a configuration of lowest potential energy. Based on quantum mechanics we now have a statistical mechanics

that leads us from molecular theory to the properties of matter in the bulk with no alarming contradictions.

"Chemical" and "Physical" Forces

The practical solutions of the problems of the interaction between the electrical systems that constitute atoms or molecules are, in general, difficult, but an important simplification has arisen from the fact that, by suitable approximation, the stable configurations may be made to fall into certain classes identifiable with the types of combining forces or bonds that the chemists have postulated by induction from their experiments, together with types of forces well known in experimental physics. Thus, in one type of configuration, the force between two atoms acts as a plain electrostatic attraction between two oppositely charged particles. This is the ionic link met with in salts such as sodium chloride. In another type of stable arrangement, we have a complex state of affairs that corresponds to the sharing of electrons between two atoms as postulated by G. N. Lewis. This is the covalent link, the common binding in organic chemistry and the formation or breaking of such bonds is what chemists usually mean by a chemical reaction. These bonds are directed and an atom can have only so many of them. Thus arise the combining laws of Dalton and the stereochemistry of van't Hoff. Another stable arrangement which was not at all understood before the quantum theory is that which gives the cohesion of metals.

Furthermore, molecules (as well as atoms) are electrical systems, and mutual interactions between their constituent charges lead to forces that hold them together or push them apart. In this class belong the "van der Waals' forces" of the older physicists or the "residual valencies" of the chemists. From the researches of Debye, London, and others, a fair amount is known about these forces. They arise from a variety of causes in which the size, the shape and the polarizability of the molecules play an important part. These are the forces most commonly encountered in non-aqueous solutions. In the light of modern knowledge and experience, however, we now recognize that any or all of the types of force enumerated above may be met with in solutions. The present status of the controversy between the "physical" and "chemical" schools may be summed up, therefore, by the phrase, "both are partly right."

I must mention, however briefly, one other fertile source of ideas that are applicable in a study of solutions, viz, the structure of crystalline solids, for this leads us back to the geometrical ideas of Boyle. Von Laue's discovery of the diffraction of X-rays by crystals, the

simplified theory and inspired experiment by the Braggs, the mathematical studies of the homogeneous packing of bodies in space by Schönflies, Federoff, and Pope and Barlow, and the untiring efforts of many workers in the last 30 years have given us a knowledge of how the atoms, ions, or molecules are arranged in crystals.

Hand in hand with this information about the geometry of solids has come, through studies of lattice energies, definite knowledge concerning the forces of cohesion in solids and liquids. For example, it is known that sodium-chloride crystals are held together by nondirected electrostatic forces between the charged ions which act as units together with a slight contribution from van der Waals' forces. The packing is determined by the relative sizes of the sodium and chloride ions. In diamond, on the other hand, the units (atoms of carbon) are held together by covalent bonds—the same bonds as in CH_4—and the structure in which one carbon is surrounded by four others is determined by the *direction* of these bonds. The bonds are very strong, and this accounts for the hardness of diamond and for the fact that it will not dissolve in any solvent, while sodium chloride dissolves easily in solutions of high dielectric constant.

On the other hand, an analysis of the structure of paraffin wax shows that the hydrocarbon molecule is the unit of structure. Within the molecule the carbon and hydrogen atoms are held together by very strong covalent forces, which practically neutralize each other's fields, leaving only the relatively weak van der Waals' forces to hold the solid together. This solid is weak, melts easily—it is easily soluble in other hydrocarbons like gasoline. Studies of solids have sharpened our ideas of the nature of cohesive forces and, at the same time, shown that these may be what used to be called purely chemical, as in diamond, or purely physical, as in paraffin wax or almost anything in between.

These studies have also made physical chemists conscious of geometry, of the important role played by the shape and size of atoms, molecules, or ions in determining solid structure. Many solids that are referred to as compounds but whose composition puzzled chemists in the past are now known to owe their existence to geometrical reasons, to the possibilities of packing in regular structures, rather than to the action of specific chemical bonds. It is also well recognized that congruity in the size and shape of the component ions or molecules is a most important factor in determining whether two substances shall form solid solutions. The old ideas of Boyle and Gassendi are still with us.

The application of these ideas of geometrical packing and the effect of intermolecular forces on it are now being carried over to liquids and solutions, where the determination of the molecular distribution in space is one of the most interesting problems.

CONCLUSION

We have traced in broad outline the development of the different ideas used in the theory of solutions and have seen how some of these ideas were taken from every-day experience and gradually shorn of their irrelevancies and molded into shape for quantitative use. Above all, I have tried to point out how developments in one science, viz, physics, were used in the development of a subject belonging to the cognate science of chemistry. In our excursion into the pit we have seen the remains of many muddling efforts in the past, attempts to explain complicated phenomena in terms of one or two simple ideas; we have seen, however, that each of these attempts contained a nugget of truth that is still a treasured possession in our store.

As a result of this excursion, I hope that the familiar sight of a crystal of common salt dissolving in water or sugar dissolving in a cup of tea will conjure before your mind a panorama of particles, motions, and forces. I hope that you will see the microscopic electrical systems of different sorts that constitute the ions of the salt or the molecules of the water being impelled to mix with each other in as disorderly a fashion as possible under the drive of their thermal motion, fulfilling their destiny by increasing the entropy of the universe. I hope that you will imagine these microcosms arranging themselves in positions of lowest energy into configurations that may sometimes suggest that they are joined by directed chemical bonds, sometimes that they are held by non-directed physical forces of varying magnitude, sometimes joined by a bond that combines the qualities of both those just mentioned. In your picture I hope you will also add geometrical considerations, that you will think of the sizes and the shapes (including the electrical distributions) of the ions or molecules and that you will note the effect of geometry on the energy (the forces) and the entropy (the motion) of the system as a whole. Above all, I hope that you will realize that the phenomenon you are witnessing differs from others you may have studied in that you can not get an explanation that will satisfy you if you exalt any one of these considerations to the exclusion of the others. Therein lies the complication.

I have left you with a picture of complexity, but if you will look to the hole of the pit whence it was digged, you will not be dismayed

by it. In the past, mathematicians have forged out of human experience methods of mechanical and exact development of ideas; they are still doing so and we have every reason to believe that mathematical methods for handling complicated problems where abstraction is undesirable will be available in the future. Our glimpse into the past gives us every assurance that a better understanding of solutions will come as time goes by, but we must expect that understanding to be based on concepts that are still further removed from our every-day experience.

BOTANY.—*New United States grasses.* JASON R. SWALLEN, U. S. Bureau of Plant Industry.[1]

Of the eight new species herein described, five are from the collections of W. A. Silveus in Florida (*Andropogon rhizomatus, A. niveus, A. sericatus*), Texas (*Sporobolus silveanus*), and Arizona (*Sporobolus patens*). *Sporobolus pulvinatus* and *Muhlenbergia villosa* are described from material previously referred to *S. pyramidatus* (Lam.) Hitchc. and *M. thurberi* Rydb., respectively, and *Glyceria cookei* is based on a collection of William Bridge Cooke from the Mount Shasta region of California.

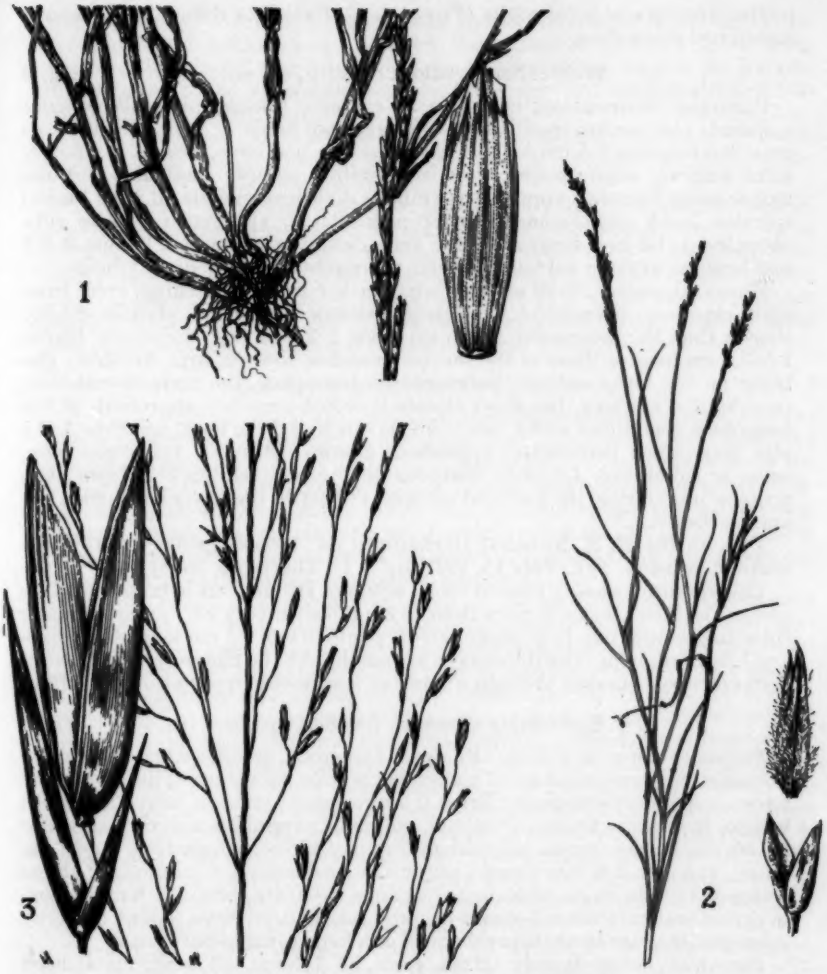
Glyceria cookei Swallen, sp. nov. Fig. 1

Perennis; culmi 15–30 cm alti, graciles, foliosi, erecti basi decumbentes, glabri; vaginae internodiis multo longiores, inferiores breves superiores elongatae, carinatae, scaberulae, marginibus hyalinis; ligula 5–7 mm longa, hyalina; laminae 3–5 cm longae, 2–3 mm latae, abrupte acutae marginibus scabris; paniculae 6–12 cm longae, simplices; spiculae breviter pedicellatae appressae vel anguste adscendentes, 15–18 mm longae; gluma prima 1.8–2.2 mm longa, obtusa, obscure 1-nervis; gluma secunda 3–3.5 mm longa, obtusa; lemmata 4–4.5 mm longa, 7-nervia, scabra, dentata, marginibus hyalinis; palea lemmate paulo longior, sulcata, bifida carinis alatis; antherae 0.8 mm longae.

Perennial; culms 15–30 cm tall, slender, leafy, erect from a decumbent branching base, glabrous; sheaths much longer than the internodes, the lower ones short, the upper ones somewhat elongate, keeled, scaberulous, the margins thin and hyaline; ligule conspicuous, 5–7 mm long, thin and hyaline; blades 3–5 cm long, 2–3 mm wide, abruptly acute, the margins finely scabrous; panicle 6–12 cm long, erect, unbranched; spikelets short pedicellate on the main axis, appressed or narrowly ascending, 15–18 mm long; first glume 1.8–2.2 mm long, oblong, obtuse, obscurely 1-nerved; second glume 3–3.5 mm long, similar to the first; lemma 4–4.5 mm long, 7-nerved, the nerves prominent, scabrous between the nerves, obtuse, irregularly dentate, the tip and margins hyaline; palea as long as or a little longer than the lemma, sulcate, bifid, the keels narrowly winged; anthers 0.8 mm long.

Type in the herbarium of the U. S. National Arboretum, no. 98480, collected in a wet place on alluvial gravel in the Box Canyon of the Sacramento

[1] Received February 27, 1941.



Figs. 1–3.—New species of United States grasses, plants and panicles, ×1, spikelets, ×10: 1, *Glyceria cookei;* 2, *Muhlenbergia villosa;* 3, *Sporobolus silveanus.* Drawings from the type specimens by Mrs. Frances C. Weintraub.

River near Mount Shasta City, Calif., altitude 3,000 feet, July 12, 1940, by William Bridge Cooke (no. 15312).

Glyceria cookei belongs to the section *Euglyceria*, in which the spikelets are linear and nearly terete. The known species of this group are all rather tall erect grasses with simple flaccid culms and relatively broad elongate blades. This species, however, has short, firm culms, decumbent and branching at the base, with short, narrow, spreading blades. It is evidently most nearly

related to *Glyceria occidentalis* (Piper) J. C. Nels. but differs in the above mentioned characters.

Muhlenbergia villosa Swallen, sp. nov. Fig. 2

Perennis, rhizomatosa; culmi 10–20 cm alti, ramosi, puberuli, obscure nodulosi; vaginae internodiis breviores, glabrae; ligula 1–2 mm longa decurrens; laminae 2.5–3.5 cm longae, eae ramorum breviores, firmae, involutae, infra glabrae, supra pubescentes, marginibus scabris; paniculae 2–4 cm longae ramis brevibus appressis vel infimis divaricatis usque ad 1 cm longis; spiculae 2–2.5 mm longae breviter pedicellatae, appressae; glumae subaequales, 1–1.6 mm longae, acutae vel subobtusae, 1-nerves; lemma 2–2.5 mm longum, acutum vel mucronatum, marginibus infra medium villosis.

Perennial; culms 10–20 cm tall, wiry, rather freely branching, erect from scaly rhizomes, puberulent, obscurely nodulose roughened; sheaths mostly shorter than the internodes, glabrous; ligule 1–2 mm long, decurrent; blades 2.5–3.5 cm long or those of the shorter branches shorter, firm, involute, glabrous on the lower surface, pubescent on the upper, the margins scabrous; panicles 2–4 cm long, the short closely flowered branches appressed, or the lowermost sometimes stiffly spreading as much as 1 cm long; spikelets 2–2.5 mm long, short pedicellate, appressed; glumes subequal, 1–1.6 mm long, acute or subobtuse, 1-nerved, scabrous on the keel; lemma 2–2.5 mm long, acute or mucronate, the keel and margins villous on the lower half; palea villous on the keels.

Type in the U. S. National Herbarium, no. 1386596, collected 15 miles south of Stanton, Tex., July 11, 1928, by B. C. Tharp (no. 5048).

This species is closely related to *M. villiflora* Hitchc. but is larger in all its parts. The latter is rarely more than 10 cm tall with very wiry culms, arcuate spreading blades 0.5–1 cm long, narrow panicles 0.5–1.5 cm long, and spikelets 1.5–2 mm long. The differences are small, but the characters of *M. villiflora* are very constant through a series of specimens from various localities.

Sporobolus silveanus Swallen, sp. nov. Fig. 3

Perennis; culmi 85–115 cm alti, dense caespitosi, erecti, scabri; vaginae internodiis longiores, glabrae vel scaberulae in collo pubescentes, inferiores confertae, superiores elongatae; ligula 0.5 mm longa; laminae usque ad 45 cm longae, involutae, firmae, flexuosae, glabrae, marginibus scabris; paniculae 30–50 cm longae, ramis adscendentibus paucifloris, inferioribus 10–15 cm longis; spiculae 5–6 mm longae, purpureae, pedicellis 5–8 mm longis; gluma prima 3–4.5 mm longa, acuminata, secunda subacuta, lata, 4.5–6 mm longa, in carina scabra; lemma 5–6 mm longum, subacutum; palea lemma aequans, subacuta, obscure carinata; antherae 4 mm longae, nigro-purpureae.

Perennial; culms densely tufted, erect, 85–115 cm tall, scabrous at least toward the summit; leaves mostly crowded toward the base, those of the culm one or two with elongated sheaths; sheaths much longer than the internodes, glabrous or scaberulous, pubescent on the collar, the lower ones firm, straw-colored, shiny, the margins spreading and more or less papery with age; ligule erose-ciliate, 0.5 mm long; blades firm, flat or usually involute, glabrous on both surfaces with scabrous margins, those of the innovations elongate as much as 45 cm long, 1–2 mm wide, curved or flexuous, those of the culms much shorter, the uppermost 7–20 cm long; panicle narrow, mostly 30–50 cm long (or shorter on more slender culms) the branches ascending, rather distant, few-flowered, naked toward the base, the lower ones mostly 10–15 cm long; spikelets 5–6 mm long, purple, the pedicels 5–8 mm

long, appressed or somewhat spreading; glumes acuminate, scabrous on the keel, the first 3–4.5 mm long, 1-nerved, the second broader, 4.5–6 mm long, 3-nerved; lemma 5-6 mm long, subacute; palea about as long as the lemma, subacute, scabrous toward the tip, the keels obscure; anthers about 4 mm long, blackish purple.

Type in the herbarium of the U. S. National Arboretum, no. 98476, collected in open woods about 10 miles northeast of Orange, Tex., September 30, 1940, by W. A. Silveus (no. 6441).

This species is closely related to *Sporobolus floridanus* Chapm. and *S. teretifolius* Harper, the former differing in having flat blades as much as 5 mm wide, more densely flowered panicles, smaller spikelets 4–5 mm long with nearly equal glumes and the latter in having smaller panicles 15–25 cm long, pilose in the axils, and slightly smaller spikelets with a narrower first glume which is usually less than half as long as the second. The long sparsely flowered panicles of large purple spikelets are very striking and characteristic.

Sporobolus pulvinatus Swallen, sp. nov. Fig. 4

Annuus; culmi 5–30 cm alti, caespitosi, basi decumbentes, glabri: vaginae internodiis breviores, glabrae, in ore plusminusve hispidae; ligula ciliata, 0.5 mm longa; laminae 4–7 cm longae, 2–5 mm latae, utrinque scabrae, ea suprema multo reducta; paniculae 2–8 cm longae, pyramidatae, ramis verticillatis appressis vel divaricatis, basi nudis, densifloris; spiculae 1.5–1.7 mm longae, breviter pedicellatae, appressae; gluma prima minuta; gluma secunda et lemma aequalia, abrupte acuta vel subobtusa; palea lemma aequans, minute dentata; antherae 0.3 mm longae, pallidae.

Annual; culms 5–30 cm tall in small or rather dense tufts, decumbent spreading at the base, glabrous; sheaths shorter than the internodes, glabrous, more or less hispid at the throat; ligule ciliate, about 0.5 mm long; blades mostly 4–7 cm long, 2–5 mm wide or smaller in depauperate plants, lanceolate-acuminate, scabrous on both surfaces and on the thick white margins, the uppermost much reduced; panicles 2–5 cm or rarely as much as 8 cm long, pyramidal, the branches verticillate, appressed, spreading at maturity, naked at the base, densely flowered, with scattered but rather prominent glandular areas, and a large pulvinus at the base of each; spikelets 1.5–1.7 mm long, short pedicellate, appressed; first glume minute; second glume about as long as the spikelet, abruptly acute or subobtuse; lemma similar to the second glume but somewhat narrower; palea broad, conspicuous, as long as the lemma, minutely dentate; anthers 0.3 mm long, pale or pinkish; caryopsis 1 mm long, asymmetrically obovate, pale lead colored or reddish, the embryo appearing as a blackened area at the base.

Type in the U. S. National Herbarium, no. 997877, collected at Adamana, Ariz., August 6–15, 1903, by David Griffiths (no. 5107).

This species has been confused with *Sporobolus pyramidatus* (Lam.) Hitchc. but is easily distinguished by its annual habit, short flat blades, and abruptly acute or subobtuse second glume and lemma. *S. pyramidatus*, described from South America (as *Agrostis pyramidatus*), is a strong densely tufted perennial with stiff, erect, acuminate blades and spikelets as much as 2 mm long. The second glume and lemma are gradually acute or subacuminate rather than acute or subobtuse, as in *S. pulvinatus*.

Sporobolus pulvinatus is apparently rather common on sandy plains and roadsides of northern Mexico, extending northward to Texas, New Mexico, and Arizona, where it is relatively rare, at least as indicated by herbarium specimens, and southward to Oaxaca. Specimens representing this species are as follows:

TEXAS: El Paso, *M. E. Jones 4338;* without locality, *Reverchon.* NEW MEXICO: Valencia County, 50 miles west of Albuquerque, *John Redd* in 1935 (Soil Conservation Service no. 755); San Ysidro, Sandoval County, *Dean Mahaffey 83.* ARIZONA: Wilcox, *Griffiths 1896;* Benson, *Griffiths 1490.* SONORA: Agiabampo, *Palmer 814* in 1890; Guaymas, *Palmer 696* in 1887; Batamotal, *Orcutt* in 1899; Imeris to Santa Ana via Magdalena, *Griffiths 6856* CHIHUAHUA: Chihuahua, *Pringle 816.* COAHUILA: Saltillo, *Hitchcock 5580.* TAMAULIPAS: Tampico, *Hitchcock 5789.* SINALOA: Mazatlan, *Purpus 359.* DURANGO: Durango, *Hitchcock 7583, Palmer 384* in 1896; Bernejillo, *Johnston 7787.* QUERÉTARO: Querétaro, *Hitchcock 5855.* HIDALGO: Pachuca, *Hitchcock 6758.* ZACATECAS: Villa de Cos, *Johnston 7427.* OAXACA: Tomellin, *Hitchcock 6236.*

Sporobolus patens Swallen, sp. nov. Fig. 5

Annuus; culmi 10–25 cm alti, graciles, erecti, glabri; vaginae internodiis breviores, glabrae, in ore sparse hispidae, ea suprema elongata aphylla; ligula ciliata, 0.5 mm longa; laminae 1–2 cm longae, 1–2 mm latae, lanceolatae, planae, marginibus scabris; paniculae pyramidales, 2.5–5 cm longae, ramis paucifloris patentibus infimis subverticillatis superioribus alternis, ramulis abrupte patentibus; spiculae 1.8–2 mm longae, pedicellibus divaricatis usque ad 3 mm longis; gluma prima 0.3 mm longa; gluma secunda et lemma aequalia, acuta; palea lemmate paulo brevior, lata, truncata, minute dentata; antherae 0.2–0.3 mm longae; caryopsis 1 mm longa, pallida.

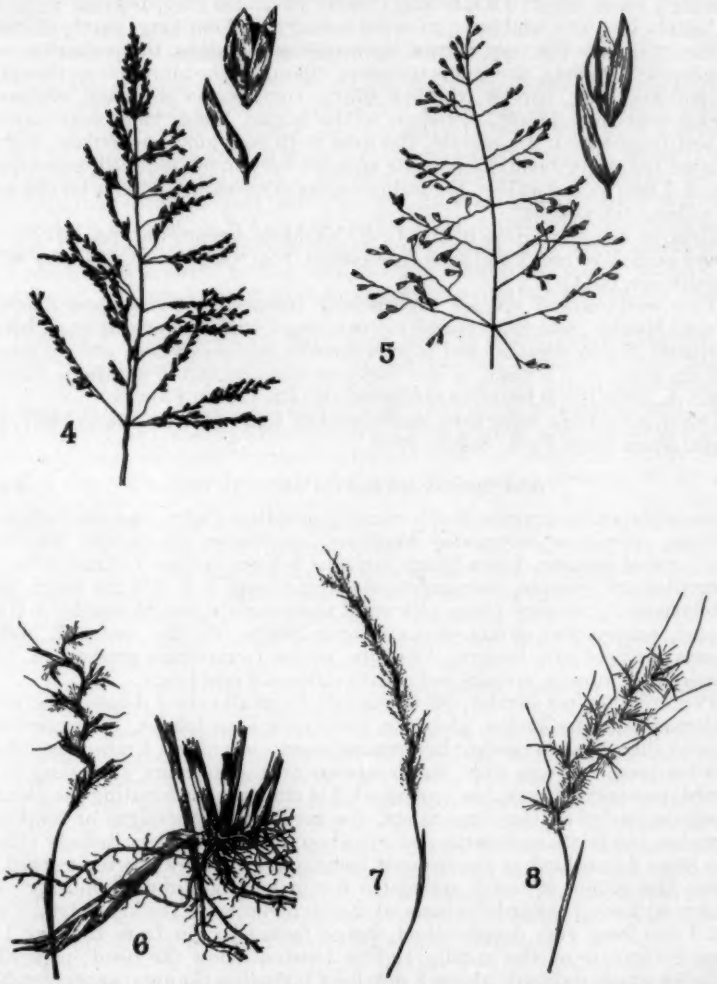
Annual; culms 10–25 cm tall, slender, erect, in small tufts, glabrous; sheaths shorter than the internodes, the upper one elongate almost bladeless, glabrous, sparsely hispid at the throat; ligule ciliate, about 0.5 mm long; blades 1–2 cm long, 1–2 mm wide, lanceolate, flat, scabrous on the margins; panicles pyramidal, 2.5–5 cm long, the slender branches spreading or even reflexed, the lower ones subverticillate, the upper ones scattered, few flowered, the branchlets abruptly spreading; spikelets 1.8–2 mm long, the pedicels slender, spreading, as much as 3 mm long; first glume minute, about 0.3 mm long; second glume and lemma equal, acute, the lemma a little broader than the glume; palea somewhat shorter than the lemma, broad, truncate, minutely dentate; anthers minute, 0.2–0.3 mm long, pinkish; caryopsis 1 mm long, pale.

Type in the U. S. National Herbarium, no. 1723881, collected at Wilcox, Ariz., September 26, 1938, by W. A. Silveus (no. 3504).

Probably closely related to the preceding, differing in having very slender culms, delicate few-flowered panicles, long spreading pedicels, and larger spikelets. The pulvini are inconspicuous and there are no glandular areas on the axis or branches of the panicle.

Andropogon rhizomatus Swallen, sp. nov. Fig. 6

Perennis, rhizomatosus; culmi 50–70 cm alti, solitarii vel caespitosi, glabri, in parte superiore ramosi, ramis gracilibus appressis vel adscendentibus; vaginae internodiis longiores, obscure carinatae, glabrae, inferiores aphyllae; ligula membranacea, minute erosa, 0.5 mm longa; laminae 10–25 cm longae, 1–3 mm latae, glabrae; spathae angustae inconspicuae; racemi solitarii, 2–3 cm longi, pedunculis gracilibus 3–7 cm longis; rachis tortuosa marginibus villosis; spicula sessilis 5–6 mm longa, gluma prima apice obscure carinata, glabra; lemma fertile 5 mm longum, angustum, arista 8–10 mm longa, geniculata, infra geniculam contorta; spicula pedicellata reducta, 2–3 mm longa, exaristata, pedicello superne ciliato.



Figs. 4–8.—New species of United States grasses, plants and panicles, ×1, spikelets, ×10: 4, *Sporobolus pulvinatus;* 5, *Sporobolus patens;* 6, *Andropogon rhizomatus;* 7, *Andropogon niveus;* 8, *Andropogon sericatus.* Drawings from the type specimens by Mrs. Frances C. Weintraub.

Perennial; culms 50–70 cm tall, slender or rather stout, scattered, or in small dense tufts, erect from short scaly rhizomes, glabrous, rather sparingly branched above the middle, the usually long slender branches appressed or narrowly ascending; sheaths much longer than the internodes, or the upper ones shorter, rounded on the back or obscurely keeled, the lowermost short, crowded, bladeless, but these not always evident; ligule membranaceous,

minutely erose, about 0.5 mm long; blades 10–25 cm long, 1–3 mm wide, flat or loosely involute, glabrous; racemes solitary, 2–3 cm long, partly enclosed or exserted from the very narrow inconspicuous spathes, the peduncles very slender, 3–7 cm long, the rachis tortuous, villous on the margins; sessile spikelet 5–6 mm long, narrow, the first glume rounded on the back, obscurely keeled near the summit, glabrous; fertile lemma 5 mm long, very narrow, awned from about the middle, the awn 8–10 mm long, geniculate, tightly twisted below the bend; pedicellate spikelet very much reduced, inconspicuous, 2–3 mm long, awnless, the pedicel arcuate spreading, villous on the margins above the middle.

Type in the herbarium of the U. S. National Arboretum, no. 98478, collected in shallow rocky soil near Homestead, Fla., October 16, 1940, by W. A. Silveus (no. 6614).

This well-marked species superficially resembles *Andropogon stolonifer* (Nash) Hitchc., which is typically much larger with longer rhizomes, broad, distinctly keeled sheaths, and more numerous racemes which are commonly 4–6 cm long. It is a plant of low rocky or alkaline soil of southern Florida, while *A. stolonifer* is found in sandy woods of northern Florida.

Other collections have been made west of Palm Beach, *Silveus 6661*, and Royal Palm State Park, *Silveus 6606*.

Andropogon niveus Swallen, sp. nov. Fig. 7

Perennis; culmi graciles 50–65 cm alti, caespitosi glabri; vaginae carinatae, glabrae, inferiores internodiis longiores, superiores internodiis breviores; ligula membranacea, 1 mm longa; laminae 5–9 cm longae, 1–2 mm latae, divergentes vel reflexae, marginibus scabris; racemi 4–7, 3–4 cm longi, rachi subflexuosa densissime pilosa pilis ca. 2 mm longis; spiculae sessiles 5–6 mm longae, suberectae; gluma prima minute bifida, obscure carinata, glabra; lemma fertile 4 mm longum, lobatum, arista 1 cm longa, geniculata, infra geniculam contorta; spicula pedicellata reducta 3 mm longa.

Perennial; culms slender, 50–65 cm tall, in small rather dense tufts, erect, glabrous; sheaths keeled, glabrous, the lower ones longer, the upper ones shorter than the internodes; ligule membranaceous about 1 mm long; blades 5–9 cm long, 1–2 mm wide, flat, scabrous on the margins, spreading to reflexed; racemes solitary, few to several, 3–4 cm long, terminating the slender, elongate, rather distant branchlets, the rachis nearly straight or somewhat flexuous, the joints and sterile pedicels about 5 mm long, very densely villous, the hairs 2 mm long at the summit becoming gradually shorter toward the base; first glume of sessile spikelet 5–6 mm long, glabrous, minutely bifid, obscurely keeled toward the summit, 2-nerved between the keels; fertile lemma 4 mm long, very deeply lobed, awned from near the base, the awn 1 cm long, geniculate at the middle, tightly twisted below the bend; pedicellate spikelet much reduced, about 3 mm long including the awn; anthers yellow, 2.5 mm long.

Type in the herbarium of the U. S. National Arboretum, no. 98477, collected on sandy land about 15 miles south of Kissimmee, Fla., October 21, 1940, by W. A. Silveus (no. 6684).

This very graceful species is allied to *Andropogon gracilis* Spreng., which can be distinguished by the longer involute blades, more conspicuously hairy racemes, and stouter longer awns as much as 2 cm long. It is rather common in open sandy pineland of central Florida. Other collections than the type have been made in Florida east of Clermont, Lake County, *Silveus 6704;* Gainesville, Alachua County, *Swallen 5634, 5639;* 8 miles east of Dundee,

Polk County, *McFarlin 3707;* Brooksville, Hernando County, *H. R. Reed* in 1933.

Andropogon sericatus Swallen, sp. nov. Fig. 8

Perennis; culmi graciles, 50–80 cm alti, erecti, caespitosi, in parte superiore multiramosi, ramis gracilibus erectis vel adscendentibus; vaginae glabrae, carinatae, internodiis breviores; ligula membranacea, truncata, 1 mm longa; laminae innovationes subfiliformae, 10–20 cm longae, supra ad basin pilosae, eae culmorum 15–20 cm longae, 2–3 mm latae, conduplicatae marginibus scabris; spathae inconspicuae; pedunculi 4–6 cm longi, gracillimi, curvati; racemi solitarii, 3 cm longi, vix exserti; rachis gracilis, flexuosa, dense pilosa pilis usque ad 7 mm longis; spicula sessilis 5 mm longa, divergens; gluma prima sulcata carinis scabris; lemma fertile 3 mm longum, bilobum, arista 15–20 mm longa, geniculata, infra geniculam contorta; spicula pedicellata reducta, 3–4 mm longa.

Perennial; culms 50–80 cm tall, rather slender, tufted, erect, glabrous, profusely branching in the upper half, the slender branches and racemes forming a somewhat dense but delicate inflorescence; sheaths, except the lower ones, shorter than the internodes, keeled, glabrous; ligule membranaceous, truncate, 1 mm long; blades of the innovations very narrow or subfiliform, 10–20 cm long, long pilose on the upper surface toward the base; culm blades broader, 2–3 mm wide, conduplicate, mostly 15–20 cm long, scabrous on the margins; spathes very inconspicuous; peduncles 4–6 cm long, very slender, curved but becoming straight with age; racemes solitary or rarely paired, 3 cm long, scarcely exserted from the spathes, the rachis slender, flexuous, conspicuously hairy, the hairs at the summit of the joints as much as 7 mm long, gradually shorter downward, the sterile pedicels spreading, hairy like the rachis joints; sessile spikelets 5 mm long, spreading; first glume conspicuously keeled with a deep furrow between the scabrous keels; lemma 3 mm long, bilobed, awned from just below the middle, the awn 15–20 mm long, geniculate, tightly twisted below the bend; pendicellate spikelet very much reduced, 3–4 mm long including the awn.

Type in the herbarium of the U. S. National Arboretum, no. 98479, collected on Ramrod Key, Fla., October 17, 1940, by W. A. Silveus (no. 6633).

The relationship of this grass is not evident. The racemes are mostly solitary as in the section *Schizachyrium,* but occasionally they are paired as in the section *Arthrolophis,* thus breaking down the primary character used to separate *Schizachyrium* as a genus. Superficially this species resembles larger plants of *A. gracilis* Spreng., the racemes of which are fewer and much more conspicuously hairy, and all the blades are involute. The numerous slender branches forming a relatively dense but delicate inflorescence, and the usually solitary, flexuous, silky racemes are characteristic.

ZOOLOGY.—*A review of the snakes of the genus* Ficimia.[1] HOBART M. SMITH, Smithsonian Institution, and EDWARD H. TAYLOR, University of Kansas. (Communicated by HERBERT FRIEDMANN.)

In 1936 Taylor[2] reviewed most of the species of *Ficimia* known from Mexico, including a very distinct new species discovered by him in Sonora (*desertorum*). This review was based on material available in the EHT-HMS collection and of necessity was not complete.

While the collection of the U. S. National Museum also lacks certain species (*desertorum, quadrangularis, ruspator*), it does contain a number of specimens that present new and noteworthy information on distribution and variation of other species in the genus. This material, combined with that now present in the EHT-HMS collection, makes possible a redefinition of the several species and an evaluation of certain specific and generic characters of species and groups of species.

Two groups are apparent in *Ficimia* (*sensu lato*), one (*olivacea* group [=*Ficimia, sensu stricto*]) containing *publia, variegata,* a new species described below as *ruspator, olivacea,* and *streckeri,* the other (*cana* group [=*Gyalopion*]) containing *cana, quadrangularis,* and *desertorum.* The association of the latter with the *cana* group is open to question, since the species has two characters that (if normal) distinguish it from all others, not only of the group, but of the genus (entire anal, a loreal[3]). However, it agrees with the *cana* group in pattern and in having the rostral separated from the frontal by contact of the prefrontals. The latter is one of the chief characteristics of the *cana* group, and since *desertorum* seems to be directly ancestral to the other two species of the group, there is little gained by placing it in another group or genus.

The two groups differ from each other in contact (or separation) of the rostral from the frontal and in number of ventrals and subcaudals. The *olivacea* group has the rostral in contact with the frontal, ventrals 140 to 160, and caudals 32 to 42. The *cana* group has the rostral separated from the frontal by contact medially of the two prefrontals, and has 129 to 146 ventrals and 23 to 36 caudals. No hemipenial differences are discernible, and differences in dentition are slight (see following discussion).

The members of the *olivacea* group are differentiated by variations

[1] Published by permission of the Secretary of the Smithsonian Institution. Received January 30, 1941.

[2] Taylor, E. H., Proc. Biol. Soc. Washington, 49: 51–54. 1936.

[3] The entire anal may not be normal, as one specimen of *publia* has it the same. The loreal is not completely unique, either, as one *cana* possesses a loreal (see Fig. 16).

in pattern (presence, absence, number, and width of blotches), by presence or absence of internasals, and by number of postoculars. Every member (with one exception) has a distinctive pattern, which fortunately is subject to less intraspecific variation (without interspecific overlap, so far as now known) than the two varying characters of scutellation (which do overlap interspecifically). Accordingly pattern is the primary medium of differentiation in the process of speciation in the genus. Scutellation is more generally constant throughout the group, is less readily affected than pattern, and differentiations that have occurred in it are less well stabilized. In both pattern and scutellation, however, there is a definite, orthogenetic trend toward reduction and simplification.

In the *cana* group also pattern is the chief medium of species differentiation. *F. cana* and *quadrangularis* are differentiated from each other largely by pattern characters resulting from two different modes of reduction from a pattern type such as possessed by *desertorum*. Differentiation in scutellation has also occurred, however, and by the same process (simplification by fusion, the loreal of *desertorum* rarely present in *cana* and *quadrangularis*, fused with the prefrontal), carried out during long periods of isolation (i.e., separation from parent stock), as in the *olivacea* group. In both pattern and scutellation *desertorum* is the most primitive of the group. If we regard this species as representing a type ancestral to the other two species, then the two orthogenetic trends evident in the *olivacea* group are quite as obvious in the *cana* group.

In the center of dispersal of the *olivacea* group is *publia*, which we believe is the most primitive of that group, since it is the only one normally with internasals; its pattern is also one from which the other pattern types conceivably may have been derived. The trends of evolution in the group are toward elimination of the blotched pattern (through production of many small spots) and fusion of the head scales. Essentially two lines of divergence, each showing these trends of evolution, from the *publia* stock, are evident: one on the Atlantic coast, marked by extremes of fusion of head scales and of pattern reduction, and one on the Pacific coast, marked by lesser pattern reduction and little fusion of head scales. The Pacific coast branch is now split into two geographic (and specific) populations, one south (east) of the Isthmus of Tehuantepec (*variegatus*), the other north (west) of the Isthmus (*ruspator*). In the Isthmus itself is *publia*. In this line pattern reduction has proceeded but little; the dorsal spots are well defined, and only more numerous and a little narrower than

in *publia*. In scutellation also little change has occurred, the northern form retaining the scutellation of *publia*, the southern form losing the internasals (by fusion with the prefrontals).

Two species (*streckeri* and *olivacea*) have emerged from the Atlantic coast branch also, but in this the pattern is totally eliminated in one (*olivacea*), nearly so in the other (*streckeri*); both have lost the internasals, and *streckeri* marks the extreme in structural specialization in the genus by fusion of the two postoculars.

In the *cana* group, by its possession of a loreal and a generalized pattern, *desertorum* should be ancestral to *cana* and *quadrangularis*; its central geographic position in Sonora supports this view. Its entire anal (apparently a specialized character) may have developed after the evolution of *cana-quadrangularis* stock (in which case each stem possesses a specialized character in scutellation), or unfortunately it may be an aberrant character appearing in the single known specimen.

It is obvious from the foregoing discussion that two widely different stocks, long isolated from each other, are at present included in *Ficimia*, in the arrangement proposed by Boulenger (Cat. Snakes, vol. 2, 1894). These have different centers of dispersal (Fig. 11), different ranges, and different morphological characters, and while obviously related their common ancestry seems very remote. They are units possessing the characters defining them as genera according to present usage of that term; they fit that definition much better than some genera at present generally recognized. Accordingly the eight species of these two units are segregated in the genera *Gyalopion* and *Ficimia*.

Genus **Gyalopion** Cope

Gyalopion Cope, Proc. Acad. Nat. Sci. Philadelphia, 1861, p. 243.

Genotype.—*Gyalopion canum* Cope, *loc. cit.*, by monotypy.

Diagnosis.—Maxillary teeth 12 to 15, subequal, no diastemata, some with very distinct, shallow, lateral depressions, all or most others with some evidence of same; body short, cylindrical, head not distinct from neck; eye small; pupil round; snout projecting, pointed; rostral large, separated from frontal by prefrontals; internasals present; loreal present or absent; anterior section of nasal usually fused with first labial; one anterior temporal; posterior chinshields very small; scales smooth, with single apical pits; ventrals 129 to 146; caudals 23 to 36; hemipenis undivided, distal half or two-thirds calyces, a small adjacent (proximally) area spines, basal sixth ridges, sulcus single.

Remarks.—Because of the constant presence of internasals, presence of a loreal in two specimens, and constant separation of the rostral from the frontal, this genus is, in general, more primitive than *Ficimia*. That it is not directly ancestral to it is attested by the peculiar pattern, reduced ventral and caudal count, and peripheral distribution (with a different center of dispersal).

Gyalopion desertorum (Taylor) Figs. 2, 7, 15

Ficimia desertorum Taylor, Proc. Biol. Soc. Washington 49: 51–52. 1936 (12 kilometers northwest of Guaymas, Sonora); Kansas Univ. Sci. Bull. 24: 494, pl. 43, fig. 1. 1936 (1938).

Diagnosis.—Rostral separated from frontal by prefrontals; a loreal; anal single (normal?); blotches entirely black on middorsum; nuchal spot extending onto frontal and supraocular region; ground color reddish, except on middorsum.

Specimens examined.—One, the type, the only known specimen (EHT-HMS 4576).

Remarks.—From *canum* and *quadrangularis* this species differs by possessing a loreal, perhaps in having a single anal, and in color pattern. The latter is more like that of *quadrangularis* than *canum*, since in both the spots are uniform black (not brown, black-edged as in *canum*) and the nuchal spot is fused across the middorsal occipital region with another black spot on the top of head which involves the frontal and extends laterally through and below the eyes.

In *quadrangularis*, however, the spots are less numerous (26 on body, 5 on tail; in *desertorum*, 32 on body, 8 on tail), and they are restricted to the middorsal region, the sides being unmarked. In *desertorum* the blotches extend laterally to the edge of the ventrals, but on the sides of the body a broad, central area of each scale in the blotches is light, the dark area restricted to the edges of the scales. Only the nuchal blotch is uniform black on the sides of the body.

The reddish (magenta) dorsal ground color (cream on middorsum) of *desertorum* is a very noteworthy and surprising development. This color is very striking in life, although not evident after six years in preservative: the local residents called the snake a coralillo. Since red occurs in no other species of either *Gyalopion* or *Ficimia* (so far as now known; *quadrangularis* may have it), its significance is not readily obvious. Presumably it is a specialization.

The maxilla has 13 subequal teeth, most of them feebly grooved laterally; extreme anterior tip toothless.

The hemipenis is 10 caudals long; distal three caudal lengths calcyces; adjacent five caudal lengths spines, the size increasing proximally; two large basal spines; remaining area at base ridged, each ridge surmounted by tiny spines; sulcus single.

G. desertorum differs from all others of its genus and of *Ficimia* (so far as known) in the presence of tiny spines on the proximal portion of the hemipenis, and by the presence of a loreal (latter not completely unique). With some reason the species could be separated in a monotypic genus, especially if the single anal proves constant. We have refrained from doing so because it appears to be directly ancestral to *canum* and *quadrangularis*.

Gyalopion quadrangularis (Günther)

Ficimia quadrangularis Günther, Biol. Centr. Amer., Rept., p. 99, pl. 35, fig. A. 1893 (Presidio, near Mazatlán, Sinaloa).

Diagnosis.—Rostral separated from frontal by prefrontals; no loreal; anal divided; no spots on sides of body, only markings a series of 26 rounded or subquadrangular, uniform blackish-brown spots on body, 5 on tail; spots not extending below fifth scale row, sides of body below this nearly white; nuchal spot confluent with interocular dark bar.

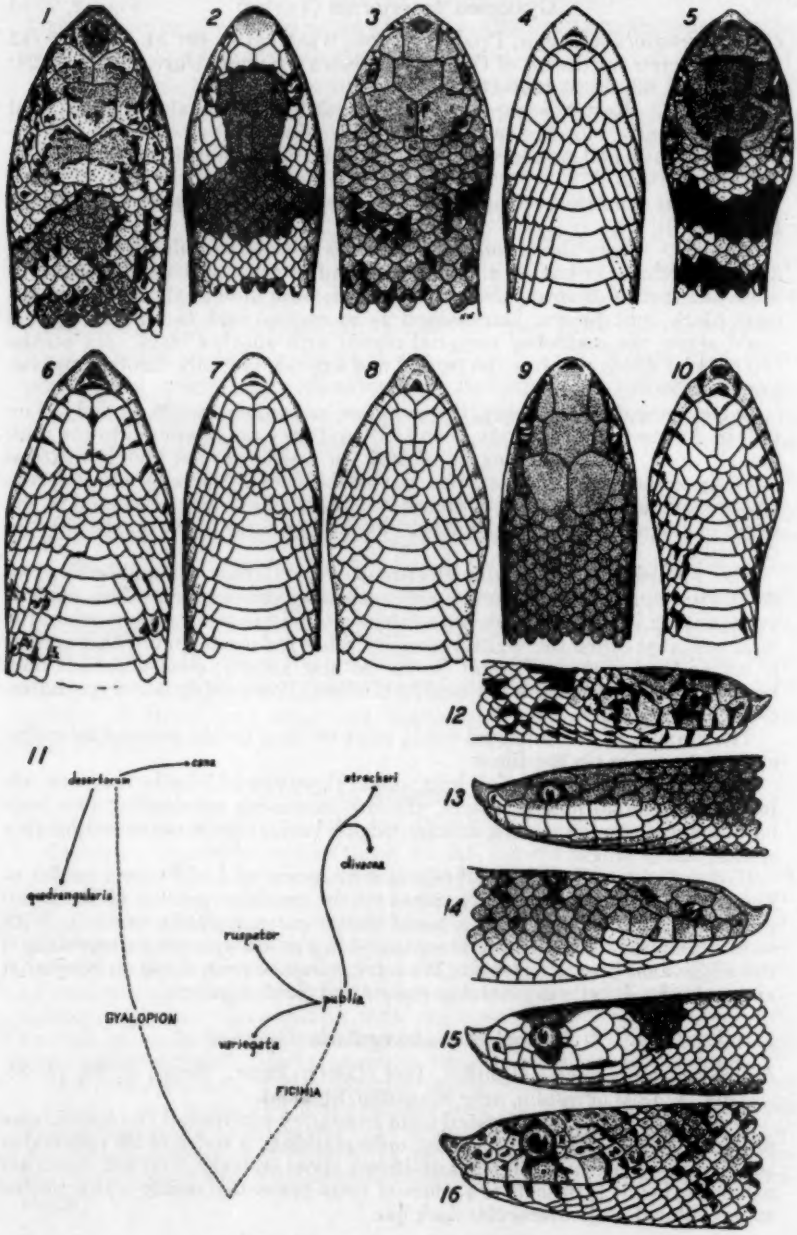


Fig. 1.—(See opposite page for legend).

Specimens examined.—None. Apparently none in American museums; type in British Museum.

Remarks.—This species does not differ from *canum* in scutellation. Günther points out that the seventh labial is very small, but the size of this scale varies greatly at least in *Ficimia publia*, and possibly also in *quadrangularis*. Some *publia* have it considerably smaller than the tertiary temporals (as in *quadrangularis*), others have it much larger.

Pattern differences from *canum* are obvious; spots fewer (30 to 39 in *canum*), head markings black, fused with first nuchal spot (not in *canum*), no marks on sides (secondary spots on sides in *canum*, dorsal spots also extending on sides), all spots black (brown, black-edged, in *canum*). It has fewer spots than *desertorum*, and the spots are restricted to the middorsal region, but otherwise it is much like the latter, from which its pattern obviously is derived.

Gyalopion canum Cope Figs. 1, 6, 16

Gyalopion canum Cope, Proc. Acad. Nat. Sci. Philadelphia, 1860, p. 243 (Fort Buchanan, Ariz.; U.S.N.M. nos. 16427–8).

Ficimia cana Garman, Mem. Mus. Comp. Zool. 8: 83, 161. 1883; Van Denburgh, Occ. Papers California Acad. Sci. 10: 777–779. 1922; Taylor, Copeia, 1931, no. 1, pp. 4–5.

Diagnosis.—Rostral separated from frontal by prefrontals; no loreal; anal divided; spots on body 30 to 39, on tail 9 to 12; spots brown, black-edged, broken laterally or continuous with lateral spots, reaching nearly to ventrals; irregular, small spots scattered on sides of body.

Specimens examined.—Four.

Range.—Southeastern Arizona east to Tom Green County, Tex.; south to the Chisos Mountains, Tex. Not yet recorded from Mexico.

Locality records.—ARIZONA: Fort Buchanan (U.S.N.M. nos. 16427–8); Montezuma Canyon, Huachuca Mountains (Van Denburgh). NEW MEXICO: White Sands, Alamogordo (Van Denburgh); 10 miles north of Florida, Luna County (Kans. Univ. nos. 6616–7). TEXAS: Green Gulch, Chisos Mountains (U.S.N.M. no. 103654); Tom Green County (Baylor Univ. no. 6015); El Paso (Van Denburgh).

Remarks.—The color pattern of this species is markedly different from that of the other two species of the genus in having the blotches light-centered and black-edged, and a different head and neck pattern. An interocular dark bar, bordered by light anteriorly and posteriorly, is visible in this species; a similar bar extends across the middle of the parietals; the nuchal blotch does not extend onto the head. The pattern is conceivably derived from that of *desertorum*, in which the blotches number about the same, but are solid black. The

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Figs. 1, 6, 16.—Cephalic scutellation of *Gyalopion canum*, from K.U. no. 6616, Florida, N. M. Loreal and small lower preocular not usually present.

Figs. 2, 7, 15.—Cephalic scutellation of *Gyalopion desertorum*, from holotype, EHT-HMS no. 4576, Guaymas, Sonora.

Figs. 3, 8, 14.—Cephalic scutellation of *Ficimia streckeri*, from holotype, K.U. no. 9140, Rio Grande City, Tex.

Figs. 4, 9, 13.—Cephalic scutellation of *Ficimia olivacea*, from EHT-HMS no. 4575, Tierra Colorada, Veracruz.

Figs. 5, 10, 12.—Cephalic scutellation of *Ficimia ruspator*, from holotype, EHT-HMS no. 23646, Tixtla, Guerrero.

Fig. 11.—Diagrammatic representation of the possible phylogeny of *Gyalopion* and *Ficimia*.

latter feature seems to be the primitive condition in *Ficimia* as well as in *Gyalopion*, since southern (presumably most primitive) *publia* have the spots nearly or quite solidly black.

TABLE 1.—VARIATION IN GYALOPION CANUM

Number	Sex	Ventrals	Caudals	Supral.	Infral.	Proc.	Ptoc.	Ptoc.	Body spots	Tail spots
6617	♂	134	35	7-7	7-7	1-1	1-2	1-1	39	12
103654	♂	136	30	7-7	7-7	1-1	2-2	1-1	34	12
5284	♀	136	27	7-7	7-8	1-1	2-2	1-1	30	9
6616	♀	143	31	7-7	8-8	2-2	2-2	1-1	36	9
6015	♀	141	31	7-7	7-7	1-1	2-2	1-1	36	11
Brit. M.	♀	131	28	7-7		1-1	2-2	1-1		
Ruthven	♀?	145	29	7-7	7-8	1-1	2-2	1-1	40	9

Maxilla with 12 teeth, all with moderately distinct to faint, lateral depressions or grooves; tip toothless.

Hemipenis (of K.U. no. 6617) about 14 caudals long; distal half calyces, these extending a little farther proximally along sulcus; nearly all of remainder spines; two large basal spines; extreme basal portion ridged, without spicules.

One specimen (no. 6617) has the first labial completely separated from the nasal. Another from the same locality has a loreal and a small, lower preocular (Fig. 16).

Genus **Ficimia** Gray

Ficimia Gray, Cat. Snakes Brit. Mus., p. 80. 1849.

Amblymetopon Günther, Cat. Snakes Brit. Mus., p. 7. 1858 (genotype, *variegatum*, by monotypy).

Genotype.—*Ficimia olivacea* Gray, *loc. cit.*, by monotypy.

Diagnosis.—Like *Gyalopion*, except: Maxillary teeth with very faint lateral grooves or depressions; rostral in contact with frontal, separating prefrontals medially; loreal absent; internasals present or absent (fused); ventrals 140 to 160, caudals 32 to 42.

Ficimia publia Cope

Ficimia publia Cope, Proc. Acad. Nat. Sci. Philadelphia, 1866, p. 126 (Yucatán; two cotypes, U.S.N.M. nos. 16427–8); Barbour and Cole, Bull. Mus. Comp. Zool. **50**: 153. 1906; Taylor, Proc. Biol. Soc. Washington **49**: 53. 1936; Schmidt and Andrews, Field Mus. Nat. Hist., zool. ser., **20**: 173–174. 1936; Hartweg and Oliver, Univ. Michigan Mus. Zool. Misc. Publ. **47**: 23. 1940.

?*Ficimia olivacea* (*sensu lato*, *nec* Gray) Stuart, Univ. Michigan Mus. Zool. Misc. Publ. **29**: 51. 1935.

Ficimia variegata (*nec* Günther) Taylor, Proc. Biol. Soc. Washington **49**: 54. 1936.

Diagnosis.—Rostral in contact with frontal; internasals usually present (84 percent); two postoculars, or if only one, the other obviously fused with it or with supraocular; a dorsal pattern of distinct blotches or irregular bands, 21 to 35 on body, 7 to 11 on tail; centers of blotches usually lighter, edges black (all black only in southern [Honduras] specimens); length of blotches equal to two to four scale lengths; spaces between blotches never exceeding one and one-half times length of blotches, usually equal or less.

Specimens examined.—Fourteen. Partial data on four others.

Range.—Isthmus of Tehuantepec to western Honduras; on Pacific slopes only from the Isthmus of Tehuantepec to southern Guatemala.

Locality records.—CHIAPAS: La Esperanza, near Escuintla (U.S.N.M. no. 110296). OAXACA: Ranchero Pozo Río (U.M.M.Z. no. 82594); La Concepción (U.S.N.M. no. 110298); Tehuantepec (U.S.N.M. no. 110297). VERACRUZ: Minatitlán (Taylor). YUCATÁN: Catmis (F.M.N.H. no. 26993); Chichen Itza (F.M.N.H. nos. 20623, 20653; M.C.Z., Barbour and Cole); Yucatán (U.S.N.M. nos. 16427–8; Brit. Mus.). GUATEMALA: ?La Libertad (U.M.M.Z., Stuart); Piedras Negras (U.S.N.M. no. 110295); Escuintla (U.S.N.M. 12688). HONDURAS: Ceiba (U.S.N.M. nos. 55237–8, 64986). One other record is Cuernavaca, Morelos (Brit. Mus.). While this may be correct, its distant removal from other localities represented by the species makes it questionable, until supported by other locality data. If the locality is correct, the specimen very likely may be referable to *ruspator*. It has internasals.

Remarks.—It is our belief that the chief character identifying this species and separating it from its nearest relatives is its pattern. It has less numerous blotches than *variegata* and *ruspator* (which have nearly identical patterns), and much broader and more regular ones than *streckeri; olivacea* has none.

The head markings show a great deal of variability. They are symmetrical and well defined in the Tehuantepec specimens, absent in the Honduras specimens, and present, although asymmetrical and not well defined, in the others.

The presence or absence of internasals is not an infallible, invariable character in this group. While *publia* is generally characterized by internasals present, the fact that one specimen has one internasal partially fused with the prefrontal and another specimen has one internasal on one side, leads us to believe that the two specimens lacking internasals on both sides are merely variants of *publia*. The latter two specimens show no differences in pattern, and no differences we can consider significant in scutellation, from other *publia*. Both occur within the expected range of *publia*.

Species in which the internasals have been lost do not show a variation like that which occurs in *publia:* 14 specimens of these species (*streckeri, olivacea, variegata*) show the occurrence of an internasal but once (on one side of one *olivacea*). Since the trend in this genus is toward loss of these scales, it is to be expected that the variation should occur in those retaining the scales distinct (*publia, ruspator*), not in those in which they are lost; distinct internasals are an anomaly in the latter, but the lack of them in the former is merely evidence of a well-established generic trend. This fact is one of the chief reasons that *ruspator* is held distinct from *variegata*, which is known to normally lack internasals (none in four specimens).

As shown in Table 2, the relative width and length of frontal, rostral, and frontal-rostral suture seem to have no great significance in *publia*, except that the frontal-rostral suture may be broader in younger specimens, and that the rostral is generally a little shorter than the frontal.

If other forms are distinguished in the future among the specimens here referred to *publia*, we believe they will be subspecies distinguished by features of the color pattern. The most distinct population now discernible is that of Honduras; the three specimens from that country have the blotches bandlike and of uniform color throughout, the ground color light (not darkened), and very few lateral marks. All other *publia* have the blotches distinctly light centered; the condition of the Honduras specimens is closely

TABLE 2.—VARIATION IN FICIMIA PUBLIA

Number	Sex	Ventrals	Caudals	Supral.	Infral.	Proc.	Ptoc.	Intern.	Rostrofrontal suture	Rostral width	Rostral length	Frontal length	Body spots	Tail spots	Gen. loc.
									mm	mm	mm	mm			
55237	♂	144	38	7–7	8–8	1–1	2–1	0–1	0.9	2.0	2.3	3.0	28	9	Honduras
55238	♂	144	39	7–7	7–8	1–1	2–1	1–1	1.0	1.9	2.8	3.1	31	10	Honduras
Stuart	♂	135	36												Peten
110295	♂	146	38	7–7	8–8	1–1	2–2	1–½	1.2	2.8	4.0	4.0	27	8	Peten
16428	♂	134	33	7–7	7–7	1–1	2–2	1–1	0.7	2.0	2.8	2.8	31	11	Yucatán
26993	♂	136	37	7–7	7–7	1–1	1–2	0–0					25	8	Yucatán
M.C.Z.	♂?	145	37					1–1					26	9	Yucatán
Brit. M.	♂?	142	36			1–1	2–2	1–1							Yucatán
82594	♂	143	36	7–7	7–7			1–1					25	8	Tehuantepec
64986	♀	156	35	7–7	7–8	1–1	1–2	1–1	0.9	1.8	2.1	2.9	30	9	Honduras
16427	♀	138	30	7–7	7–8	1–1	2–2	1–1	0.7	1.9	2.6	2.7	31	10	Yucatán
20623	♀	148	35	7–7	7–7	1–1	2–2	1–1					26	9	Yucatán
20635	♀	151	32	7–7	6.7	1–1	2–2	1–1					25	7	Yucatán
Rickard	♀	155	34	7–7	7–7	1–1	1–1	0–0			5.1	4.4	32	9	Veracruz
110297	♀	148	32	7–7	7–7	1–1	2–2	1–1	1.7	1.9	2.0	2.2	21	7	Tehuantepec
110298	♀	152	37	7–7	8–8	1–1	2–2	1–1	1.0	1.8	2.0	2.2	25	7	Tehuantepec
110296	♀	153	36	7–7	7–8	1–1	2–2	1–1	1.2	2.8	4.5	3.8	31	8	Chiapas
12688	♀	154	32	7–7	8–8	1–1	2–2	1–1	0.9	2.1	3.8	3.5	35	9	Guatemala
Brit. M.	♀	142	35					0–0							"Mexico"

approached by the Piedras Negras specimen, in which the blotches are almost entirely black. We have refrained from naming the Honduras specimens because it appears certain that, if they are recognized, then the remainder of *publia* should be split: the Yucatán specimens have few marks on the sides; the Escuintla specimen has the blotches bandlike; and the remainder have the blotches split laterally (not forming crossbands), numerous lateral spots, and adults have the ground color darkened. Until these pattern types are known from many more specimens, and the limits of variation can be more definitely established, it is impossible to diagnose subspecies in *publia* with any degree of certainty.

Ficimia ruspator sp. nov. Figs. 5, 10, 12

?Ficimia publia Boulenger, Cat. Snakes Brit. Mus. **2**: 271. 1894. (*part.;* the Cuernavaca specimen).

Holotype.—E. H. Taylor–H. M. Smith collection no. 23646, female, 3 miles east of Tixtla (about 10 miles east of Chilpancingo), Guerrero.

Diagnosis.—Similar to *Ficimia publia*, but blotches on body 43, on tail 11. Similar to *Ficimia variegata*, but internasals present. Two postoculars; blotches narrow, tending to be light-centered; ventrals 154; caudals 33.

Description of holotype.—Rostral large, elongate, its suture with frontal subequal to sutures between latter and prefrontals; rostral sharply upturned anteriorly, the ridge bordered posteriorly by a shallow depression; length of rostral from anterior ridge to frontal (2.3 mm) distinctly greater than length of frontal (2.0 mm), very slightly greater than length of median parietal suture; nasal narrow, anterior section fused with first labial; prefrontal in contact with second labial; preocular single, large; two postoculars, lower

smaller; one elongate, narrow, anterior temporal; two (three) tertiary temporals; seven supralabials, all relatively high, sixth largest, fourth next largest, third and fourth contacting orbit, seventh slightly larger than lower tertiary temporal; diameter of orbit nearly as great (five-sixths) as its distance from labial border, little less than half its distance from tip of snout; seven infralabials, fourth largest, three in contact with anterior chinshields; posterior chinshields practically indistinguishable, separated medially by two scales, somewhat larger than gular scales, in contact with two labials.

Scales in 17 rows throughout, smooth, with single apical pits; ventrals 154; anal divided; caudals 33. Total length 144 mm; tail 20 mm.

Color.—General color light gray; body with 43 transverse, black blotches, some of the anterior blotches with dimly lighter (brown) centers; blotches broken on sides of body at about fifth scale row; below this sides with irregular black spots and vertical streaks, some rarely confluent with dorsal blotches, some involving ends of ventrals; spaces between blotches about equal to length of blotches or slightly less (one and one-half to two scale lengths, middorsal line); tail with 11 dorsal crossbars, sides with a very few spots. Top of head somewhat brownish gray, with numerous irregular black marks; a large dark spot under eye, reaching lip; labial sutures dark. Infralabial sutures dark stippled, the markings not distinct; no other gular marks; some spots on sides of body involving ends of ventral; a little scattered stippling on sides of belly; otherwise ventral surfaces unspotted, white.

Remarks.—Aside from the "Cuernavaca" record of Boulenger, which is open to much doubt, the type of *ruspator* is the only specimen of *Ficimia* known from the Pacific slopes of Mexico north (west) of Tehuantepec. The fact that this area faunistically is much different from the area in Chiapas and southeastern Oaxaca inhabited by *variegata;* that the range of the latter species is separated from the presumed range of *ruspator* by an area (Tehuantepec) occupied by *publia;* that species of *Ficimia normally* lacking internasals very rarely (if ever) have them on both sides (it is the reverse that frequently occurs); and that *Ficimia* tends to differentiate in each different area it inhabits, leads us to believe that the single specimen and type of *ruspator* may be normal and represent a form different from *variegata* (by presence of internasals) and *publia* (by more numerous blotches). If further specimens prove to lack internasals usually, then the concept of the range of *variegata* must be extended to include this area, in spite of the fact that it is split in the Tehuantepec area by the range of *publia.* That we do not believe this will prove to be the case is implied by the fact that the Guerrero specimen is here named. We believe that *ruspator* and *variegata* are of independent origin (from *publia,* however), and that the parallelism between the two in pattern is explicable by the orthogenetic trend in the genus toward reduction in size and increase in number of the blotches. Probably *streckeri* passed through the same stage in its pattern evolution, which in it has gone still farther and produced very narrow, irregular bands. The fact that *variegata* has lost the internasals while *ruspator* retains them indicates a possibly greater age for the former.

The parallelism between *ruspator* and *variegata* is remarkably similar to that occurring in *Conophis lineatus* and *C. pulcher.*

Ficimia variegata (Günther)

Amblymetopon variegatum Günther, Cat. Snakes Brit. Mus., pp. 7–8. 1858 (Mexico).

?Ficimia olivacea Steindachner, Sitzb. Akad. Wiss. Berlin **61**: 19. 1870; Günther, Biol. Centr. Amer., Rept., p. 98. 1893 (part), pl. 35, fig. C; Boulenger, Cat. Snakes Brit. Mus. **2**: 272. 1894 (part).

Diagnosis.—Rostral in contact with frontal; apparently no internasals normally; two postoculars normally; pattern consisting of 45 to 56(?) band-like blotches on body, about 16 on tail; bands covering one and one-half to two scale lengths medially; spaces between bands about equal to length of bands.

Specimens examined.—One. Four known.

Range.—Mountains of central Chiapas and eastern Oaxaca (i.e., east of the Isthmus of Tehuantepec).

Locality records.—The single specimen examined is from Guichicovi, Oaxaca. If the Steindachner specimen from "Tustla" is properly associated with this species, the locality more correctly may be Tuxtla Gutierrez, Chiapas (as previously stated by one of us Taylor, *loc. cit.*, 1936, p. 54]). The cotypes collected by Sallé very likely came from this same region, as a number of other species of reptiles collected by him are now known to be restricted to that area.

Remarks.—If *variegata* has any significance whatever, the name must be applied to specimens with a large number of dorsal blotches. The fact that the four specimens now known with numerous blotches all appear to have originated from a rather well-defined area not occupied by other members of the genus (except perhaps *olivacea*, the range of which may overlap that of *variegata*), correlated with the fact that all four lack internasals while the species' closest relatives (*publia*, *ruspator*) normally have them (in spite of the general trend in the genus toward elimination of them), indicates a natural association and not a purely arbitrary one.

The specimen examined has 48 bands on the body, 16 on the tail. Descriptions of other specimens of the species unfortunately do not make clear whether the band count given is the total number or only those on the body. The figure in Günther (Biol. Centr. Amer.) of one of the cotypes shows about 45 on the body, about 16 on the tail (total 61). However, Günther states that there are "51 to 56 of these crossbars," but leaves indefinite what these numbers represent. Since neither number corresponds either to body or total blotches shown in the figure, perhaps the latter is incorrectly executed. The original description does not clarify the situation, as the specimen described in detail is merely said to have "56 black narrow cross bars."

The Guichicovi specimen is a female; ventrals 152; caudals 36; supralabials 7–7; preoculars 1–1; postoculars 1–2 (upper fused with supraocular on one side); no internasals; rostro-frontal suture 1.2 mm; rostral width 2.7 mm; rostral length 3.8 mm; frontal length 3.9 mm. The two specimens in the British Museum (a juvenile and a female) have 160 and 149 ventrals, respectively, 37 and 36 caudals; both have 1–1 preoculars and 2–2 postoculars.

Ficimia olivacea Gray Figs. 4, 9, 13

Ficimia olivacea Gray, Cat. Snakes Brit. Mus., p. 80. 1849 (Mexico); Sumichrast, La Naturaleza **6**: 41. 1882; Taylor, Proc. Biol. Soc. Washington **49**: 52–53. 1936.

Diagnosis.—Rostral in contact with frontal; internasals normally absent; two postoculars, or if only one, the other obviously fused with it or with supraoculars; uniform dark gray or brown above, no evidence of transverse markings.

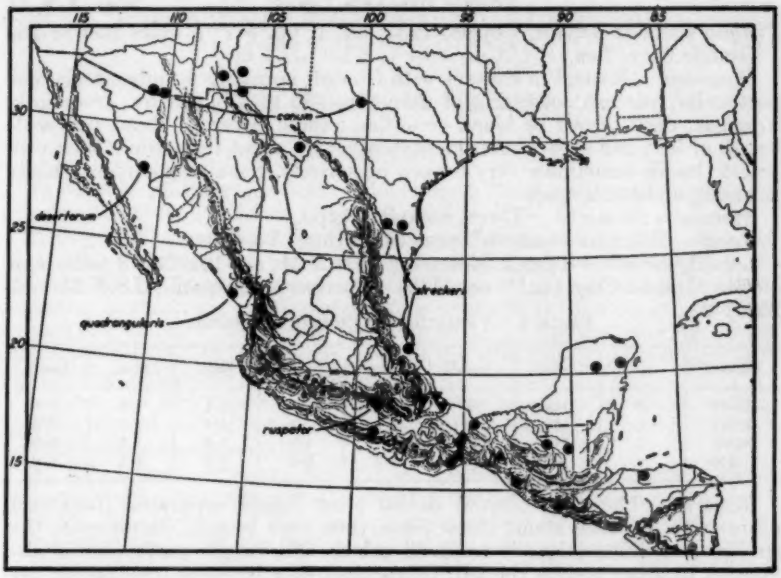

Fig. 17.—Geographic distribution of the species of *Gyalopion* and *Ficimia*. Inverted triangles, *olivacea;* triangles not inverted, *variegata;* solid circles not otherwise indicated, *publia*.

Specimens examined.—Four. Two others reported.

Range.—Central and southern Veracruz in coastal regions and low hills (not to coast in extreme southern Veracruz); northeastern Oaxaca.

Locality records.—OAXACA: El Barrio, near Lagunas (U.S.N.M. no. 30131). VERACRUZ: Orizaba (U.S.N.M. no. 6329); Otopa (F.M.N.H. no. 1315); Tierra Colorada (EHT-HMS 2194).

Remarks.—The species is well defined, since it is the only one without dorsal spots.

TABLE 3.—VARIATION IN FICIMIA OLIVACEA

Number	Sex	Ventrals	Caudals	Supral.	Infral.	Proc.	Ptoc.	Intern.
6329	♂	140	37	7-7	7-7	1-1	2-2	0-0
Brit. M.	♂	152	42			1-1	2-2	0-0
Brit. M.	♂	150	41			1-1	2-2	0-1
2194	♂	142	38	7-7	7-7	1-1	2-2	0-0
30131	♀	146	37	7-7	7-7	1-1	2-2	0-0
1315	♀	142	37	7-7	7-7	1-1	2-2	0-0

Maxilla (no. 6329) with 15 subequal teeth, almost all with moderately well defined, lateral grooves. Hemipenis of same specimen nine caudals long, distal half calyces; nearly all of remainder with spines, increasing in size proximally and terminating with two larger basal spines; extreme basal portion ridged, spineless; sulcus single.

Ficimia streckeri Taylor Figs. 3, 8, 14

Ficimia streckeri Taylor, Copeia, 1931, no. 1, pp. 5–7 (3 miles east of Rio Grande City, Tex.).

Diagnosis.—Rostral in contact with frontal; normally no internasals; one postocular; pattern consisting of numerous (38 to 47), narrow, frequently irregular, dark brown or black cross-bars; these covering about one scale length or less, and separated from each other by about three times their own length; bands sometimes very broken posteriorly, remaining evident chiefly as small, middorsal spots.

Specimens examined.—Three, including type.

Range.—Extreme southern Texas to northern Veracruz.

Locality records.—TEXAS: Edinburg (U.S.N.M. no. 101051); 3 miles east of Rio Grande City (K.U. no. 4140). VERACRUZ: Tuxpam (U.S.N.M. nos. 25201–2).

TABLE 4.—VARIATION IN FICIMIA STRECKERI

Number	Sex	Ventrals	Caudals	Supral.	Infral.	Proc.	Ptoc.	Intern.
25201	♂	144	37	7–7	7–7	1–1	1–1	0–0
25202	♀	149	29	7–7	7–7	1–1	1–1	0–0
101051	♀	143	33	7–7	7–7	1–1	1–1	0–0
4140	♀	144	30	7–7	8–8	1–1	1–1	0–0

Remarks.—The very narrow, dorsal cross bands, separated from each other by a distance about three times their own length, characterize this species and differentiate it from all others. The single postocular is also unique. In other species the two postoculars may be fused together, or one fused with the supraoculars, but in all such cases the fusion is obvious.

KEY TO GYALOPION AND FICIMIA

1. Rostral separated from frontal ..... *Gyalopion* 2
   Rostral in contact with frontal ..... *Ficimia* 4
2. Dark markings on head and middorsum brown, black-edged; head markings variable, not a single large blotch fused with first nuchal spot ..... *G. canum*
   Dark markings on head and middorsum uniform black; a large black spot on head, fused with first nuchal spot 3
3. Markings restricted to middorsum, not extending onto sides of body; 26 spots on body; no loreal ..... *G. quadrangularis*
   Markings extending onto sides of body to ends of ventrals; 32 spots on body; a loreal ..... *G. desertorum*
4. No dorsal markings whatever; usually two postoculars; usually no internasals ..... *F. olivacea*
   Dorsal bands present; one or two postoculars; internasals present or absent 5
5. Dorsal bands very narrow (a scale length or less), separated from each other by about three times their length; one postocular; no internasals ..... *F. streckeri*
   Dorsal bands longer (one and one half or more scale lengths), separated from each other by no more than one and one half times their length; two postoculars usually; internasals present or absent 6
6. Bands on body 21 to 35; internasals usually present ..... *F. publia*
   Bands on body 43 or more; internasals present or absent 7
7. Internasals present ..... *F. ruspator*
   Internasals absent ..... *F. variegata*

PROCEEDINGS OF THE ACADEMY AND AFFILIATED SOCIETIES

PHILOSOPHICAL SOCIETY

1170TH MEETING

The 1170th meeting was held in the Cosmos Club Auditorium, Saturday, October 12, 1940, President GIBSON presiding.

Program: W. EDWARDS DEMING: *On the sampling problems of the 1940 census.*—This paper was the presentation of a joint study carried out by F. F. Stephan, Morris Hansen, and the author. Properly applied and interpreted, sampling methods are capable of yielding results that for most inquiries are as valuable as those that would be obtained on a complete coverage. Such methods were used to enlarge the scope of the 1940 census. The sample thus obtained contributes in four ways:

I. Since not every person responds to every question, the field work is speeded up and carried out at reduced cost, thus making it possible to carry more questions on the schedule.

II. Tabulations can be carried out on the sample for estimates of many population characteristics, months ahead of the regular tabulations prepared from the full count. This is an especially important feature in times of national emergency, and the fact is that several tabulations are even now in progress to obtain quick counts of the distribution of the labor force by area, sex, age, etc.

III. Because the sample tabulations can be carried out at greatly reduced cost, more cross-tabulations can be tabulated and published (i.e., more information made available) than would otherwise be possible.

IV. The sample cards can be stored for subsequent tabulations as the need arises. Storage of the cards for the complete count, even from one decade to another, is not contemplated because of the space required. Storage of the sample cards opens up the possibility, not heretofore realizable, of preserving latent information for several decades.

The sampling scheme puts one person in the sample to represent himself and 19 others. These sample persons were so chosen that the tabulations made up from their characteristics will closely approximate the proportions that would be shown by tabulations made from the entire population. The procedure, so far as the enumerators were concerned, was automatic in its operation. Care was taken to circumvent certain process biases that are inherent in a systematic coverage. The most important process biases arise from the required order of enumeration, by which, in cities, the enumerator starts at a corner and works around the block, and enumerates within each household the head, the wife, oldest child, etc., in a specified order, according to long-established census procedure. The magnitudes of these and other biases were measured by studying the records of previous censuses, in order to see which ones need to be eliminated, and just what the effect is if they are not. The method of designating the sample persons also anticipated and eliminated the effect of a number of enumerators' misunderstandings. (*Author's abstract.*)

The paper was discussed by Messrs. STEPHAN, HANSEN, TRUESDELL, SEEGER, HAWKESWORTH, and SEQUIST.

1171ST MEETING

The 1171st meeting was held in the Cosmos Club Auditorium, Saturday, October 26, 1941, President GIBSON presiding.

Program: E. D. MCALISTER, Smithsonian Institution: *Fluorescence and photosynthesis.*—Recent observations of chlorophyll fluorescence show that the intensity of fluorescence depends on the rate of photochemical processes in a living plant. In particular, when the intensity of fluorescence and rate of CO_2 assimilation were recorded simultaneously during the induction period (MCALISTER, E. D., and MYERS, JACK, Smithsonian Misc. Coll., **99**. No. 6. 1940) it was found that the two curves were nearly perfect mirror images of each other under low oxygen pressures (photosynthesis then being the predominant photochemical reaction). These data suggest the "working hypothesis" that the energy losses from chlorophyll as heat and fluorescence are affected alike by changes in photochemical processes in the plant, i.e., the ratio of heat loss to fluorescence is a constant. If the intensity of fluorescence is plotted against absorbed energy (steady state conditions) a straight line is obtained, under light limitation, the slope of which is proportioned to $(1-E)$ and E is the upper limit of the efficiency of photosynthesis. (E is the ratio of the number of quanta accepted by the photosynthetic mechanism per second to the number absorbed by the chlorophyll per second.) When photosynthesis is constant or zero a steeper line is obtained, the slope of which is independent of E. The ratio of the first slope to the latter is numerically equal to $(1-E)$. Thus, if the hypothesis previously mentioned is correct, this type of fluorescence data provides a means of measuring an upper limit to the efficiency of photosynthesis. Particularly significant are the data of Wassink (WASSINK, E. C., et al., Enzymol. **5**: 100–109. 1938; **5**: 145–172. 1939), wherein, with alga cultured under conditions such as to give high quantum yields, values of E ranging from 0.35 to 0.43 may be calculated from the slopes of his curves for fluorescence with and without poisoning of photosynthesis by cyanide and by urethane. In other words these data may be interpreted to indicate that about half of the energy absorbed by chlorophyll is lost directly as heat *even* under conditions where high quantum yields are obtained. (*Author's abstract.*)

JESSE W. M. DUMOND, California Institute of Technology: *The consistency of our knowledge concerning the atomic constants.*—The purpose of this paper was to show in greater detail the construction and use of a certain type of consistency chart already briefly described by the author in a previous paper, and by means of it to exhibit, with a few minor changes and some important new additional data, the present status of the dilemma regarding the values of e, m, and h which grows out of the discrepancy between various results of careful measurements of functions of these variables. The discrepancy itself remains practically as glaring and just as unexplained as ever. Scales have been added permitting the values of e, m, and h corresponding to any intersection point to be read off directly. (*Author's abstract.*)

The first paper was discussed by Messrs. HUMPHREYS and ABBOT; the second one by Messrs. ALLISON, BRICKWEDDE, and WENSEL.

1172D MEETING

The 1172d meeting was held in the Cosmos Club Auditorium, Saturday, November 9, 1940, President GIBSON presiding.

Program: E. TELLER: *On the expanding universe.*—The idea that the universe is populated with stars at a roughly uniform density leads to two diffi-

culties which have been recognized for a long time. First, the radiation of distant stars would result in an infinite radiation density at every point, and secondly the gravitational energy due to interaction with distant stars diverges. The fact that the universe expands shows a way out of both these difficulties; moreover, it is not necessary to draw the conclusion that divergences can be avoided only if the total number of stars is finite. The expansion of the universe is proved by red shifts in spectral lines of distant groups of stars, leading to the conclusion that any two such star groups recede with a velocity which is roughly proportional to their distance. Thus one obtains a picture of the system of stars which is somewhat analogous to a crystal in uniform thermal expansion. One may describe such expansion by considering any atom at rest and by saying that the other atoms recede from this atom as a center. The red shift caused by the recession of distant stars lowers the radiation energy received from a distant star all the more the farther the star is, thus making it possible that the total energy arriving at any point remains finite. The gravitational action of distant stars also appears in a new light. Let us consider the gravitational action of the stars within a large sphere on a star located on the surface of that sphere. The gravitational force increases with the size of the sphere, but so does the velocity of the star on the surface with respect to the average velocity within the sphere. The kinetic energy due to this relative motion is under present conditions of expansion much more than sufficient to overcome the gravitational attraction.

Considering the distribution of stars in somewhat greater detail one finds that the stars are grouped in great clusters or galaxies. Within a galaxy the stars are spaced at a few light years apart while the dimension of a galaxy is a few thousand light years. The stars of a galaxy execute motions analogous to the thermal motion of atoms in a gas. The galaxy is held together by gravitational forces and does not expand. One finds such galaxies at approximately a million light years apart rather uniformly distributed in space. The galaxies recede from each other so that in our picture of the expanding crystal the galaxies correspond to atoms. It is interesting to notice that the relative velocity of two neighboring galaxies is of the same order of magnitude as the average velocities of stars within one galaxy and also as the thermal velocities of atoms within stars. Extrapolating backward in time to states of the universe where the average density of galaxies has been greater one might be led to the idea that originally all galaxies formed one system, which in separating into star clusters gave rise to similar relative velocities of two resulting clusters as were found for the stars within a cluster. And extrapolating still further back one might suspect that the origin of stellar velocities is the separation of larger accumulations of matter into stars and that during that separation the stars obtained velocities which did not differ greatly from the thermal velocities of the atoms. Thus stellar and also galactic velocities may originate in the thermal motion of atoms which, as has been shown, can in turn be explained by the thermo-nuclear reactions that furnish the energy of the stars. (*Author's abstract.*)

L. B. TUCKERMAN: *Mathematical spoofing.*—In spite of their traditional reverence for the discipline of logical rigor, even the best of mathematicians at times indulge in spoofing.

This frequently takes the form of devising problems involving some absurdity. Many of these are included in the numerous compilations of mathematical puzzles, and when properly understood are interesting and instructive.

Examples were given of problems that were mathematically correct but

physically absurd, problems that involved mathematical inconsistencies, problems that buried the essential data under a flood of irrelevant words, and problems that were essentially indeterminate.

In the last category are the numerous problems which ask that, from a finite sequence of numbers, the next numbers in the sequence be determined. Several examples were given and their indeterminacy discussed. The logical absurdity of these tests has been pointed out by mathematicians, and mathematicians use them only when they are spoofing. However, in spite of their absurdity they are still included in many of the so-called intelligence tests, to which school children are subjected. (*Author's abstract.*)

The first paper was discussed by Messrs. HAWKESWORTH, MOHLER, BARAFF, and ROLLER; the second one by Messrs. HAWKESWORTH and PAWLING.

1173D MEETING

The 1173d meeting was held in the Cosmos Club Auditorium, Saturday, November 23, 1940, President GIBSON presiding.

Program: H. MARK, Polytechnic Institute of Brooklyn: *Modern aspects of the synthetic rubber problem.*—The production of synthetic products with rubberlike properties is not only interesting from the point of view of National Defense, but it seems to be also promising and timely from the point of view of our present fundamental knowledge on the field of Highpolymeric Substances. The lecture gives a report on the present conception of the structure of such compounds—having long, flexible chainlike molecules—and of the relations between this structure and their technical qualities. (*Author's abstract.*)

This paper was discussed by Messrs. MCPHERSON, SCHIEFER, and HUMPHREYS.

1174TH MEETING

The 1174th meeting, constituting the 70th annual meeting, was held in the Cosmos Club Auditorium, Saturday, December 7, 1940, President GIBSON presiding.

The treasurer reported that the income from dues and interest on investments was $1,240.45 and that the expenditures exclusive of investments was $994.47, less $10.30 for sale of offprints, leaving a net surplus of $256.28 on ordinary expenses. The ordinary expenses were at the rate of $3.18 per member.

The secretaries' joint report showed an active membership as of December 1, 1940, of 309, of whom the following were elected during the year: C. I. ASLAKSON, JOHN C. BURLEW, PETER A. COLE, TOBIAS DANTZIG, MERRILL DISTAD, ERIC DURAND, FRANK R. ELDRIDGE, R. P. EYEMAN, WALTER E. SCOTT, and IRWIN VIGNESS. The following were elected in 1939 and qualified in 1940: VINTON C. FISHEL and DWIGHT F. WINDENBURG.

The following officers were declared elected for the year 1941:

President, H. E. MCCOMB; *Vice-presidents,* W. G. BROMBACHER and R. J. SEEGER; *Recording Secretary,* FRED L. MOHLER; *Treasurer,* W. E. DEMING; *Members-at-Large of the General Committee,* G. E. BENNETT and PAUL A. SMITH.

At the conclusion of the business part of the program Dr. VANNEVAR BUSH, president of the Carnegie Institution of Washington, spoke on *Science in national defense.*

RAYMOND J. SEEGER, *Recording Secretary.*

1175TH MEETING

The 1175th meeting was held in the Cosmos Club Auditorium, Saturday, December 21, 1940, President MCCOMB presiding.

Program: W. J. ECKERT, U. S. Naval Observatory: *Scientific computation with the aid of punched cards.*—Scientists faced with extensive calculations have usually used one of three modes of attack: (1) to proceed without delay along the conventional lines, (2) to design a special machine for the purpose, and (3) to adapt to the problem devices made for other purposes. The work described here comes under the third category.

The computing laboratory in the Department of Astronomy at Columbia University employs Electric Punched Card Accounting Machines which have been modified to make them suitable for scientific computation. It was the first laboratory capable of performing general scientific calculation automatically without any reading or writing of figures. In this laboratory many classical astronomical problems, including the numerical integration of the equations of planetary motion, the solution of the main problem of the lunar theory, and the reduction of astronomical observations, have been solved.

The laboratory is now operated for the use of astronomers by the Thomas J. Watson Astronomical Computing Bureau. The bureau is a joint enterprise of the American Astronomical Society, the International Business Machine Corporation, and Columbia University.

Other similar but less complete installations such as the one at the Naval Observatory are now in use. The new Air Almanac was produced in a few months on these machines.

Slides were shown to illustrate the basic operation of the machines and their application to the computation of the apparent places of stars. (*Author's abstract.*)

T. B. BROWN: *Two-dimensional kinetic theory model.*—The "molecules" of this model consist of ping-pong balls contained in a vertical chamber formed by two glass plates which are separated only far enough to permit free motion of the balls between them. The size of this chamber (18″ wide by 24″ high) is such that the demonstrations may be seen easily by a large audience. A simple agitator-cam, working through a slot in the bottom of the chamber, keeps the balls in a state of rapid random motions.

The apparatus thus demonstrates graphically the motions of molecules as described by the kinetic theory. With the aid of various auxiliary pieces of apparatus, it was used also to illustrate the pressure of a gas against a piston, the diffusion of gas molecules through a porous plug, and Brownian motions of translation, of rotation, and of vibration. The fluctuations from average values which occur in all these phenomena are clearly illustrated and may be studied quantitatively. Such studies serve as useful experiments for the student laboratory. (*Author's abstract.*)

The first paper was discussed by Messrs. MAXWELL, GARNER, MCNISH, RAPPLEYE, DEMING, H. H. HOWE, W. DAVIS, MCCOMB, and CURTIS; the second one by Messrs. BRICKWEDDE and HUMPHREYS.

Informal communications were presented by Messrs. PAWLING and RAPPLEYE.

1176TH MEETING

The 1176th meeting was held in the Cosmos Club Auditorium, Saturday, January 18, 1941, Vice-president BROMBACHER presiding.

The Retiring President, RALPH E. GIBSON, gave an address entitled *Physical reflections in a chemical mirror.* This address is published in the present issue of the JOURNAL, pp. 325–348.

1177TH MEETING

The 1177th meeting was held in the Cosmos Club Auditorium, Saturday, February 1, 1941, President McCOMB presiding.

Program: D. R. INGLIS, Johns Hopkins University: *Motions in the earth's core.*—It is well known that the earth is gradually slowing down in its rotation, and that its axis of rotation is gradually changing in a manner that may be approximately described as a "27,000-year precession." Seismological data, while not definite on this point, indicate that the earth's core is probably rather fluid. The fact that the core is made of hot iron and nickel suggests that it is then very fluid. The question treated is whether the inner part of the core keeps up with the rotation of the solid part of the earth, or rotates about some earlier axis of rotation. Calculations based on the existence of turbulent flow in the intermediate layer, and on a drag of magnetic induction, indicate that the axes of rotation of the interior part and of the exterior probably differ in direction by one or several degrees. This involves a rather violent motion of the interior matter relative to the exterior. (*Author's abstract.*)

This paper was discussed by Messrs. HERZFELD and HAWKESWORTH.

A. B. FOCKE, Brown University: *Segregation of polonium in bismuth crystals.*—Single crystals of bismuth containing polonium as an impurity were studied to determine the distribution of the polonium. Number-distance relations for α-particles emitted normally through cleavage surfaces afford the means of investigation, measurements being made with a Geiger-point counter. When present in very small concentrations polonium is found to be segregated into small regions which have nearly regular spacing when viewed in several directions. These average spacings, 0.55 micron for planes parallel to the (111) plane and 0.86 micron for planes parallel to the $(1\bar{1}1)$ plane, are not affected by the speed of growth of bismuth crystals or by subsequent heat treatment. In the case of mechanical twinning, it is found that the spacing between polonium groups follows the crystallographic changes. (*Author's abstract.*)

1178TH MEETING

The 1178th meeting was held in the Cosmos Club Auditorium, Saturday, February 15, 1941, President McCOMB presiding.

Program: C. A. BETTS, U. S. Forest Service: *Heavy construction.*—The great variety of interesting problems encountered in heavy construction was illustrated by the following projects on which the speaker has been engaged; The six-mile Moffat Tunnel in Colorado; the $3\frac{1}{2}$ and $4\frac{1}{2}$ mile Owyhee water tunnels in Oregon, and the Owyhee Dam (the highest prior to the Boulder Dam), and smaller dams. Construction problems of the National Forest Service, including bridges, roads and fire lookout towers, were also described and illustrated. (*Abstract by the Secretary.*)

E. S. GILFILLAN, Consulting Engineer: *What happens when candy burns.*—It was shown that for the group of reactions of one chemical element with another there exists a critical series, analogous to the sum-of-states familiar in statistical mechanics, having the property that at temperatures for which the series converges the compounds break into clean fragments whereas for temperatures for which the series diverges very complex products are formed as equilibrium is approached. It is thus that charring and tar formation occur. For most pairs of elements, the temperatures of divergence are so low that no perceptible reaction would be expected to occur even in intervals long in geologic time. In the case of carbon and hydrogen, however, at the

partial pressures of hydrogen which obtain in equilibrium with mixtures of iron, iron oxides, carbon, and water vapor, the critical series diverges at temperatures at which fairly rapid reaction of these elemnts is known to occur. It was suggested that petroleum may have been formed in this way. (*Author's abstract.*)

An informal communication on *Resistivity of interstellar space* was presented by F. L. MOHLER.—It was pointed out that on the basis of recent estimates of conditions in interstellar space, the equation for resistivity of an ionized gas is applicable and the resistivity is about 0.2 ohms per cm cube. Thus interstellar space is a highly conducting medium. (*Author's abstract.*) This was discussed by Messrs. HUMPHREYS, GILFILLAN, and BRICKWEDDE.

1179TH MEETING

The 1179th meeting was a joint meeting with the Washington Academy of Sciences. Prof. P. W. BRIDGMAN, of Harvard University, delivered an address entitled *The changing position of thermodynamics.*

1180TH MEETING

The 1180th meeting was held in the Cosmos Club Auditorium, Saturday, March 1, 1941, President MCCOMB presiding.

Program: F. O. RICE, Catholic University of America: *Mechanism of chemical reactions.*—The chemist represents the reactions that he studies by equations such as,

$$C_8H_{18}+17O_2\rightarrow 8CO_2+9H_2O,$$

which represents the combustion of octane, or

$$2Na_2SO_3+O_2\rightarrow 2Na_2SO_4,$$

which represents the oxidation of sodium sulphite to sodium sulphate and occurs readily at room temperature in aqueous solution. The decomposition of acetone is represented by the equation,

$$CH_3COCH_3\rightarrow CH_4+CH_2=CO$$

which shows the formation of methane and ketene; however this occurs only at about 500°C. or higher.

All these reactions have one peculiarity in common, namely that the rate of the reaction can be profoundly influenced by the addition of relatively minute amounts of other substances. The puzzling feature is that by selecting an appropriate substance, these and many other reactions can be slowed up so that the rate can not be measured.

The present day explanation of this curious effect is that these reactions consist really of a complex series of steps in which a free radical generated initially causes a cycle of reactions in which it (or some other radical) is regenerated in each cycle and can therefore start the next cycle. It is, therefore, reasonable to expect that a substance which can combine with or destroy radicals will reduce the rate of such a reaction even if the substance is present in very small amounts. (*Author's abstract.*)

K. F. HERZFELD: *Propagation of sound in liquids.*—In liquids as in gases, sound waves consist in alternate compressions and attenuations, accompanied by temperature variations. For the same energy radiated, the pressure variation is much higher, the temperature variation lower in the liquid than in the gas.

Absorption of sound in liquids has been measured reliably up to about 80 megacycles in mercury, water, and three other liquids and turns out to be proportional to the square of the frequency. Except for mercury, it is several times larger than can be accounted for by viscosity and heat conduction. Attempts to explain this increased absorption by slowness of energy exchange between internal and external degrees of freedom seem successful for benzene, but not for water.

In liquid mixture, sound waves should produce partial unmixing, but the effect is too small to be observable. (*Author's abstract.*)

The first paper was discussed by Messrs. HUMPHREYS, CURTIS, BRICKWEDDE, HAWKESWORTH, and GIBSON; the second one by Messrs. GILFILLAN, ROCK, GIBSON, and BRICKWEDDE.

1181ST MEETING

The 1181st meeting was held in the Cosmos Club Auditorium, Saturday, March 15, 1941, President MCCOMB presiding.

Program: S. L. QUIMBY, Columbia University: *Investigations with the piezoelectric oscillator.*—The composite piezoelectric oscillator is a device which permits the measurement of the elastic constants and internal friction of single and polycrystalline solids. A small right circular cylinder of specimen material is cemented at one end to a suitably cut crystalline quartz cylinder of identical cross section. The quartz cylinder carries electrodes properly oriented with respect to the electric axes of the crystal, and a harmonically varying potential difference is maintained between these electrodes. In consequence of the harmonically varying piezoelectric stress which accompanies the electric field in the quartz, a state of forced longitudinal or torsional vibration is established in the composite system which, under these circumstances, is electrically equivalent to a series resonant circuit shunted by a capacity. The fundamental frequency of free longitudinal or torsional vibration of the composite system and the vibration decrement are deduced from the observed variation of the reactance of this circuit with frequency, and its resistance. These data, in combination with the results of corresponding measurements made on the quartz cylinder alone, yield values of the elastic constants and coefficients of internal friction of the specimen material. Particular advantages of the method are its high accuracy, economy of specimen material, and the ease with which measurements can be made at very low temperatures.

The method has been used to measure the variation of the principal elastic constants of NaCl, KCl and MgO with temperature at low temperatures, and of NH_4Cl, β-brass, and the copper-gold alloys through their transition temperatures; also, the variation of the elastic constants and internal friction of iron and permalloy with magnetization, and of nickel with magnetization and temperature through the Curie point. It has recently been extended to the treatment of non-homogeneous specimens, and studies have been made of the phenomenon of plasticity in single metal crystals. (*Author's abstract.*)

ALEXANDER HOLLAENDER, National Institute of Health: *The wavelength dependence of genetical changes produced by ultraviolet radiation.*—The results of the studies on the genetical effects of monochromatic ultraviolet radiation between 2180 and 3650A on typical fungous spores were discussed on the basis of work done in cooperation with Dr. C. W. Emmons. The technique used insured that on the average each spore received and absorbed definite quantities of energy. Survival ratios were determined from plate counts for

the different wavelengths tested. Three different types of effects were observed: (1) Toxic or fungicidal effect; (2) physiological changes, and (3) genetical changes. Fungicidal and genetical effects show a maximum of sensitivity in the wavelength range around 2600A. This wavelength is most highly absorbed by nucleic acids which are one of the main constituents of chromosomes. Genetical effects of monochromatic ultraviolet radiation have also been observed after the irradiation of liverwort sperm, pollen grain of maize, and *Drosophila* sperm. The wavelength dependence of mutation production in Drosophila is complicated by the fact that the sperm has to be irradiated with our present technique inside the living animal, and the injurious effect of ultraviolet radiation obscured the results. The significance of these findings was discussed in relation to the possible role of sunlight on the production of natural mutations. (*Author's abstract.*)

The first paper was discussed by Messrs. BARAFF, SEEGER, GOLDBERG, and TUCKERMAN; the second one by Messrs. BARAFF, MCCOMB, and MOHLER.

1182D MEETING

The 1182d meeting was held in the Cosmos Club Auditorium, Saturday, March 29, 1941, President MCCOMB presiding.

The Eleventh Joseph Henry Lecture, entitled *The constitution of diffuse matter in interstellar space*, was delivered by OTTO STRUVE, professor of astronomy at the University of Chicago. This lecture has been published in this JOURNAL **31**: 217–258. 1941.

1183D MEETING

The 1183d meeting was held in the Cosmos Club Auditorium, Saturday, April 12, 1941, President MCCOMB presiding.

Program: TOBIAS DANTZIG: *Mathematics; prospects and retrospects.*—The period through which we are now passing would be replete with tricentennial celebrations and jubilees if the world were in a mood for jubilees. Three hundred years ago modern science generally, and mathematics in particular, had come of age: the two decades from 1630 to 1650 saw the births of such important mathematical disciplines as Analytic and Projective Geometry, Infinitesimal Analysis, Theory of Equations and Theory of Numbers, Analytical Mechanics, and the Theory of Probabilities. The speaker reviewed that period, the problems which confronted it, the characters and the attitudes of the great men who launched the new sciences against the social, economic, and political backgrounds of those turbulent times, when human thought had just emerged from the oppressive influence of Scholasticism and reliance on authority. He then undertook to draw a parallel between that period and the critical times through which we are now passing. The events of the last three decades have forced upon thinking men everywhere a revaluation of values, and mathematics is no exception to this trend. The foundations of the mathematical sciences have undergone a searching critique, which few of the concepts and axioms on which these sciences rested survived unscathed. But there is also another tendency. Mathematics is an art, and as such it has not been spared the disease which has afflicted modern music, art and literature: the substitution of form for content, which was so characteristic of the Dark Ages. Whether this is but a passing malady, or augurs a decadence and a relapse into medievalism, time alone will show. However, the speaker saw definite symptoms of a healthy revolt against this sterile formalism. (*Author's abstract.*)

ARNOLD H. SCOTT: *A mechanical aid for selecting the essential terms of a determinant.*—It was shown that the method of expanding determinants whereby the rows are interchanged so that the terms of the expansion appear successively in the principal diagonal can be of material assistance in picking out wanted terms in special determinants. The determinant used for illustration was one in which all the elements of the principal diagonal had the value X except one and more than a third of the other elements were zero. The terms required in this particular problem were those containing the three highest powers of X. The rows were printed on strips of cardboard which allowed a ready interchange of the rows. Only those row interchanges were required which removed one or two X's from the principal diagonal. The terms of the expansion were then obtained from the principal diagonal in a progressive series order. (*Author's abstract.*)

The first paper was discussed by Messrs. BLAKE and SEEGER; the second one by Messrs. HAWKESWORTH, TUCKERMAN, DANTZIG, and CURTIS.

1184TH MEETING

The 1184th meeting was held in the Cosmos Club Auditorium, Saturday April 26, 1941, President MCCOMB presiding.

Program: ROBERT B. BRODE, University of California: *Cosmic-ray ionization.*—The cosmic radiation produces most of its effects at the earth's surface by the ionization along the paths of high energy charged particles. This ionization is observed by means of ionization chambers, Geiger counters, and Wilson cloud chambers. Most of the vertical coincidence counts in a pair of Geiger counters appear to be due to mesotrons. A study of the ionization along the paths of mesotrons and along the paths of electrons enables the relative mass of the particles to be estimated. The specific ionization or the total ionization produced per centimeter of the path can be obtained from cloud chamber measurements. Pictures are taken of the track after a delay of 0.1 sec. which permits the ions to diffuse slightly. With high resolution photography the individual water drops can then be counted. Each of these drops has an ion as a nucleus. Positive and negative ions can be distinguished by their motion in the clearing field or by their behavior under different expansion ratios of the cloud chamber. Electrons with an energy of a million electric volts energy have an ionization of about 45 ions pairs per cm of path. Both faster and slower electrons have greater ionization. This experimental observation agrees with the predictions of Bohr and others. Mesotrons of two hundred times the mass of an electron and with an energy of one hundred million electron volts would be expected to have about the same ionization as one million volt electrons. (*Author's abstract.*)

J. E. MAYER, Columbia University: *Statistical mechanics and liquids.*—The general methods of statistical mechanics have not been greatly changed since the time of Gibbs, although the introduction of quantum mechanics has altered many details and improved the agreement with experiment.

The general equations can be solved in only two cases, that of the gas and that of the crystal. The problem is essentially that of integration over the coordinates of some 10^{23} particles of an integrand which is the exponential of minus the potential energy of the system, divided by kT. This integration is practical only if the result can be expressed as a product of integrals over fewer coordinates. In the case of the gas, this is done by expanding the integrand into terms, the first of which is unity and gives the value of the integrand when all particles are far apart. The following terms give the corrections due to clusters of molecules which are close to each other.

In the case of the crystal, the problem is solved by assuming a configuration of minimum potential energy and expanding the integrand over very small deviations from this equilibrium position. In this case the integral becomes the product of the integrals over the so-called normal coordinates.

Neither of these two methods can be expected to work for a system at the temperature and density of a liquid. It is then necessary to find some other method of solution. One developed by Kirkwood and an analogous one developed by Mayer and Montroll appears to offer some hope. In this method one starts in the middle of the problem and works towards both ends. Distribution functions giving the probabilities of certain configurations for a small number of molecules, are introduced. The thermodynamics properties of the system can be calculated in terms of these distribution functions. By a method of successive approximations, it appears that the distribution functions themselves can be determined. (*Author's abstract.*)

The first paper was discussed by Messrs. MOHLER, P. A. SMITH, BARAFF, MAYER, BRICKWEDDE, and MCCOMB; the second one by Messrs. HAWKESWORTH, HERZFELD, and BRODE.

1185TH MEETING

The 1185th meeting was held in the Cosmos Club Auditorium, Saturday, May 10, 1941, President MCCOMB presiding.

Program: R. M. BOZORTH, Bell Telephone Laboratories: *The physical basis of ferromagnetism.*—After an introductory review of the general nature of magnetic phenomena and the magnitudes of the atomic forces involved, there was a discussion of the atomic structure of the ferromagnetic elements and elements having similar structures. This included a description of the gyromagnetic experiments and their interpretation and of atomic energy levels and exchange interaction. The properties of single crystals and the structure of domains were described in relation to the form of the magnetization curve and the nature of magnetic processes accompanying changes in field-strength. Two simple demonstrations were made of the Barkhausen effect and the directional magnetic properties of crystals. (*Author's abstract.*)

This paper was discussed by Messrs. ROLLER, BATES, KRACEK, HUMPHREYS, DORSEY, JOYCE, MCCOMB, PINEO, and MCNISH.

An informal communication was presented by PAUL R. HEYL on a law of falling bodies proposed by Galileo in *Two new sciences.* Galileo assumed that the velocity was proportional to the distance fallen and the consequences of this were discussed. This was discussed by Messrs. MCNISH and HUMPHREYS.

1186TH MEETING

The 1186th meeting was held in the Cosmos Club Auditorium, Saturday, May 24, 1941, President MCCOMB presiding.

Program: C. L. GARNER: *Recent developments in geodetic control.*—This paper consists of a brief outline of the status of the geodetic control work, particularly triangulation, in the United States at the present time, and its relation to mapping and other engineering and scientific works of national importance. It reviews very briefly the extension of the horizontal control net of the United States from its inception in 1817 to the present, showing that by far the larger part of the work as it stands today has been accomplished during the last decade. This was through the use of emergency funds for the relief of unemployment and at one time involved the employment of more than 10,000 people distributed in all of the states in carrying on ex-

tremely important work in vital areas. There is also sketched in brief the present methods of procedure in the operation of a triangulation party using steel towers, automobile trucks, and modern instruments of various types. Problems encountered in the field in carrying on the work with the required accuracy and the resulting field work are discussed in detail. (*Author's abstract.*)

HOWARD S. RAPPLEYE, *Problems in vertical control surveys.*—This paper first outlined briefly the fundamental equipment and process of spirit leveling, continued with a brief description of the precise leveling equipment and procedure of the U. S. Coast and Geodetic Survey and discussed the extent of the vertical control net. Emphasis was placed on the difficulties and problems involved in the field and office work preliminary to the publication of the final results in the form of lists of descriptions and elevations of bench marks.

The latter part of the paper discussed the difficulty of maintaining the bench marks in the field with special reference to problems involved in preventing destruction of bench marks as a result of construction, repair and maintenance activities; natural causes, such as frost heaving, rock disintegration, etc. The effect of earthquakes, regional settlement and other causes of the disturbance of bench marks were also covered briefly. (*Author's abstract.*)

The first paper was discussed by Messrs. MAXWELL, BROMBACHER, TUCKERMAN, and SMITH; the second one by Messrs. SMITH, HECK, BLAKE, H. L. CURTIS, TUCKERMAN, and MCCOMB.

FRED L. MOHLER, *Recording Secretary.*